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PHYSICOCHEMICAL PROPERTIES OF EDIBLE-CANNA AND POTATO STARCHES

BY

J. C. RIPPERTON, Chemist

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INTRODUCTION

Edible-canna (*Canna edulis*) starch has been manufactured for many years on a small scale in Queensland, Australia, but it has been used almost entirely as food. About 500 tons of the starch have been sold annually under the name of "Queensland arrowroot" largely for consumption in Australia. Small shipments have been made from time to time from Australia to Europe, but the records fail to show that any of the starch has ever been imported into the United States. As an industrial starch, therefore, it is a new product.

With the development of the edible-canna industry in Hawaii work was begun at the experiment station to discover the properties of edible-canna starch that might be helpful in determining its industrial uses, and in standardizing the process of manufacture. Since canna starch resembles potato starch more closely than it does the other commercial starches, only the potato starch was used in the comparison.

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SELECTION AND PREPARATION OF STARCH SAMPLES

A series of samples of untreated commercial potato starches, said to be typical potato starches from the Netherlands and Germany, and from the United States, were secured for test from a New York starch broker. Preliminary experiments with the potato and the canna starches showed considerable differences in their properties. For this reason it is not possible to designate any particular starch as a "typical" starch of that species. To assure inclusion in the work of starches that would vary as widely as possible in properties, selections were made from those highest and those lowest in viscosity.

Of the principal commercial potato starches used, sample No. 14 was medium in viscosity, and sample No. 56 was high. Of the principal edible-canna starches used, sample No. 5, from freshly dug rootstocks grown under dry conditions at an elevation of 400 feet, was low in viscosity; sample No. 52, from freshly dug rootstocks grown under cool, moist conditions at an elevation of 3,000 feet, was high; and sample No. 24, from the same source as sample No. 52, but the rootstocks of which were stored for 19 days before the starch was extracted, was low in viscosity.[1]

Canna-starch samples were prepared in the laboratory by the usual process of grating and washing the granules from the pulp, and by passing them through either cheesecloth or fine copper screens. They were purified by passing the wet starch through another screen (100 meshes to the inch) and then by repeated levigation with tap water until the supernatant water was clear and only a slight brown residue remained on the surface of the settled starch. The tap water used contained about 6 grains per gallon of salts in the form of sodium and calcium ions in equal amounts. The starch was dried on trays set about 2 feet above a hot plate in an open room having a temperature of about 45° C. The wet starch was air-dried in 12 to 18 hours. The canna starches thus prepared were comparatively free from impurities except for small amounts of soil particles, which are inert so far as the present study is concerned. The potato starches were also of a high degree of purity, giving no evidences of cellular tissue, of fermentation, or of having been treated with chemicals.

VISCOSITY AND SWELLING POWER

The function of starch in its many industrial uses is dependent primarily on the consistency of its solutions. In certain uses, as in the sizing of cloth and of paper, a thick-bodied solution which will only slightly penetrate the fibers is required, whereas in other uses, as in the sizing of yarns, thorough penetration of the fibers is desired and for this purpose a thin-flowing solution is necessary. The extremes vary from a limpid watery starch solution to a puttylike consistency. Other properties of starch also of importance include color, hygroscopicity, amount of cellular tissue, grit, and fermentation. However, these properties are easily determined and can be maintained practically constant under proper milling conditions. This is not true, however, of the consistency of starch solutions. Not only does the consistency of the starch solutions produced under certain conditions vary greatly, but it also is subject to continuous change.

[1] When necessary for clearness, the origin of the starches is indicated in text references to the samples. Thus, sample No. 14 is often referred to as "potato sample No. 14" and sample No. 52 as "canna sample No. 52."

NATURE OF THE STARCH GRANULE

In order to know something about the changes that take place in the starch solution, the nature of the starch granule must be understood.

A granule of untreated starch when placed in cold water and examined under the microscope shows no visible change. However, a granule that is ruptured by pressure on the cover glass, for example, will begin to swell at the point of rupture. An uninjured granule that is heated in water approximately to 65° C. or above will swell greatly, and the skin will appear to be distended and filled with translucent liquid. The interior of a granule which has been ruptured, when similarly treated, will diffuse in water and the skin will appear to be flat and shrunken.

To explain these phenomena, the starch granules have been assumed to consist essentially of two parts, an outer skin or envelope and the interior. The first part is only very slightly soluble in water, comparatively dense and heavier than water, and of a slimy consistency when heated with water. The second part is easily dispersed and forms true colloidal solutions in both cold and hot water. The envelope and the interior have been called by various names. In accordance with the terminology now in use, the envelope will be referred to in this study as "amylopectin," and the interior as "amylose." It is debatable whether these are two different chemical compounds, between which there is a sharp line of cleavage, or simply one compound with a gradual transition from one form to the other, the differences in properties being caused by difference in degree of hydration.

If untreated starch is heated in water and the diluted solution is allowed to stand, the swollen granules will settle out, leaving a clear supernatant liquid. If the volume of the swollen granules is increased by a greater concentration of starch, so that they occupy practically all the space within the solution, it will become appreciably viscous. Viscosity is lessened, however, by subjecting the solution to vigorous stirring, shaking, or grinding, and the solution becomes limpid if given severe treatment. Harrison (*5*),[2] for example, found that a potato starch with an initial viscosity of 250 was reduced to 50 by shaking the solution for one minute at 16° C., and to 20 by shaking it for the same length of time at 90°. A large proportion of the granules in such a solution will be found to have burst. Complete disruption of the granules is not so easily effected. Taylor and Beckmann (*18*), working with cornstarch, found that although some of the swollen starch granules were broken by shaking, as was indicated by a fall in viscosity, prolonged grinding in a ball mill was required to rupture them completely.

It has been said that the amylopectin fraction is wholly responsible for the viscosity of starch paste, the amylose being incapable of producing a paste, and that heating under pressure and treating with dilute acids cause the amylopectin to decompose partly. Loss of viscosity in starch solutions under such conditions is sometimes attributed to this partial decomposition. Alsberg (*2*) points out, however, that under these conditions the starch granules disintegrate on heating—the breaking of the granules rather than decomposition of the amylopectin being the cause of loss of viscosity.

[2] Italic numbers in parentheses refer to Literature Cited, p. 48.

A consideration of the physical properties of commercial starches shows that those from the cereals, such as corn, wheat, and rice, differ radically from those of the noncereals, such as potato, arrowroot, and sago. Taylor and Iddles (*19*) give the amount of amylopectin as 15.2 per cent in corn, 18.2 per cent in rice, and only 2.85 per cent in potato. Alsberg (*2*) estimates the amount of swell as 8 times for wheat, 40 times for potato, 16.5 times for edible canna, and 45 times for arrowroot. The cereal starches are thus characterized by a smaller swell, a larger proportion of amylopectin, and relatively smaller granules as compared with the noncereal starches. These factors have a marked effect on the properties and the uses of the two kinds of starches. The cereal starches tend to produce solutions of low viscosity at relatively high concentration. They are relatively stable and can be boiled or agitated to a considerable degree without marked change in viscosity. The noncereal starches, on the other hand, give viscous solutions at relatively low concentrations. They are very unstable, both boiling and agitation causing them to lose greatly in viscosity.

METHOD OF PREPARING THE STARCH SOLUTION

In view of the facts given above, the method of preparing the solution of the noncereal starch is obviously of paramount importance. Since a viscous solution can be reduced to a watery consistency either by boiling or by agitation, some arbitrary procedure in the method of solution must be closely conformed to in a comparison of different starches. Many different procedures have been used for making such comparative viscosities. Harvey (*6*) passed live steam through a water-starch suspension, at intervals drew off some of the starch solution, and determined viscosity until he obtained a constant value. The viscosity curve thus formed was considered by him as an index of the viscosity of the starch. Harrison (*5*), using a somewhat similar procedure, was unable to duplicate the results and concluded that viscosity determination is of no practical value because of the alterations produced in the solution by shaking and stirring. Wolff (*22*) brought the starch into solution on the water bath, and then boiled and stirred the mixture over a naked flame for exactly 2½ minutes. Use of these methods obviously produces a mixture of whole and broken granules. It is assumed, however, that by making close observations on the procedure in each case, the proportion of broken granules will be approximately the same, so that this value can be used as a comparative measurement of the strength of the starch. Instead of heat, sodium hydroxide is often used to swell the starch granules. However, in the use of sodium hydroxide the same difficulty exists as with heat, the granules being broken by stirring. Some investigators, working on more theoretical phases, pretreat the starch with dilute hydrochloric acid to cause the granules to break completely when they are brought into solution.

Results of preliminary investigations showed that edible-canna starch is fully as susceptible to marked changes in viscosity, due to the breaking of the granules, as is potato starch. Any method of preparation which would avoid breaking the granules or reduce breakage to the minimum would therefore be of obvious advantage. The method of procedure developed in this study for producing a uniform solution of the starch without the use of stirring or of agitation was as follows:

A series of Erlenmeyer flasks of 125-cubic centimeter capacity and of as nearly uniform weight as possible were selected for use. A variation of 10 grams or less in weight was found to have an inappreciable effect on the result. The starch sample was transferred to the flask and mixed with 10 cubic centimeters of distilled water at room temperature. The starch was brought into solution by adding hot water to the starch-water suspension from a 100-cubic centimeter pipette [3] having a large-bore tip. Keeping the tip of the pipette just below the rising surface of the solution and as near the center as possible gave the solution a uniform rolling motion, down in the center, out at the bottom, up on the sides, and in at the top. This motion kept the starch evenly dispersed while the temperature rose above the gelatinization point. Unless too great a concentration was used, all the hot water was added to the starch solution before it became too thick to roll freely. The hot water when drawn up into the pipette had a temperature of 97° C. The starch solution in the flask had a final temperature of 80°.

In order that there might be constant losses of heat, due to radiation during the process of filling the pipette and disintegrating the starch, care was taken to carry on the operations as quickly and as uniformly as possible. A 1,000-cubic centimeter rubber-stoppered flask was used for heating, and a thermometer was inserted through the rubber stopper to register the temperature in the center of the flask. Sufficient hot water was constantly added to the flask to keep the water level near the top. Careful adjustment of the heat under the flask kept the temperature within a half degree of 97° C. Final adjustment was made by heating the flask over a naked flame for a short time, the contents being swirled to assure uniformity throughout. When the water reached 97° the tip of the pipette was placed at about the center of the liquid, and 100 cubic centimeters was rapidly drawn in. The level of the water was then quickly adjusted to the mark on the stem, and the contents of the pipette were immediately delivered into the starch suspension. The final temperature of the starch solution in the flask was $80° \pm 0.5°$. Later data showed that this variation in temperature produced comparatively small differences in the results. After the starch was brought into solution a loose cotton plug was inserted in the mouth of the flask. The flask was placed at once in a water bath, fitted with an electric stirrer, and kept at 80° for 15 minutes. The level of the water in the bath was kept near the top of the flasks, which were held down by means of lead collars. After 15 minutes the starch solution was poured into the viscosimeter and viscosity was determined at 80°.

The swelling power and viscosity of potato and canna starches are greatly affected by very small concentrations of electrolytes, as will be shown later. It is important, therefore, that the distilled water be of a high and constant degree of purity. Only chemically resistant glassware should be used in making the experiment. The water left in the heated flasks should be discarded at the end of the day. In washing the glassware care should be taken to remove all traces of electrolytes resulting from cleaning mixtures. The results of all methods dealing with the swelling of starch granules are empirical.

[3] In view of the fact that the results by this method are essentially comparative rather than absolute in their nature, it is deemed unnecessary to apply corrections for volume because of the temperature changes and differences in the amount of starch used. The chief essential is uniformity of procedure.

Variation in the procedure will give a different set of results. In order to secure comparable data a given procedure must, therefore, be strictly adhered to.

The above-mentioned method is limited in its application chiefly to the noncereal starches. The cereal starches attain their maximum swell only after they have been cooked for considerable time in a temperature above 80° C. The concentration of starch necessary to produce a desirable viscosity to measure is somewhat too great to be brought into solution by this method, and usually results in the formation of lumps. Even under this procedure a certain proportion of the granules burst. (Table 19.) Bursting may have been caused by the existence of broken or ruptured granules in the raw starch as well as by the method of solution used.

METHODS OF MEASUREMENT

Two kinds of methods have been proposed for measuring the strength of a starch. One is to measure the viscosity of the starch solution with some form of viscosimeter, and the other is to determine the volume of the swollen granules.

VISCOSITY

Despite the large amount of work done on the subject by many investigators, no standard or even generally accepted method has been devised for determining the viscosity of starches, probably because of the differences existing between different classes of starch and because of the great variety of uses to which starch is put. Starches are used for some purposes as a paste. Herschel and Bergquist (*7*) state that starch in the form of paste is not viscous but plastic and should be measured as such. Nivling (*13*) states that for concentrations, such as are used in paper and textile sizing, the properties of flow, that is, the viscosity, should be measured. Over and above these considerations is the fact that starch solutions are so frail in texture and so unstable as to yield results that are not only very arbitrary but also very difficult to duplicate, particularly in the noncereal starches.

The many different kinds of instruments used in measuring the consistency of starch include the pipette type, such as the Saybolt, the Engler, and the Scott, which measure the time necessary for a given volume of liquid to pass through a standard orifice; the friction or torsional type, such as the Stormer and the MacMichael, which measure the resistance offered by the starch solution to the movement of one bounding surface with respect to the other; and, finally, the plastometer, such as the Bingham and the Greene, which measure the rate of flow of starch paste through a capillary tube under varying pressures. The kinds of instruments tested for probable use in this study were the MacMichael, the Stormer, and the Saybolt. The Stormer viscosimeter was finally adapted for use. In general, the three instruments gave similar results—the curves resulting from plotting time seconds against concentration of a number of starches showing the same general relationship in strength of starch.

All measurements were made at 80° C. Relatively low concentrations gave better duplication for potato and for canna starches, and a 70-gram weight gave the most convenient speed for measurement.

A graph was obtained by plotting time seconds against the known values in centipoises of sucrose solutions of varying concentrations which were used as the standardizing solution. This graph was subsequently used to convert the time-second values obtained for starches into centipoises.

In order to show the relative accuracy of the viscosity method as carried out in the station laboratory, a series of viscosity concentration determinations were made on the several starches at intervals over a period of one month. Often several determinations made in succession gave very closely agreeing results, but similar determinations made the following day gave another set of results. Table 1 shows the differences found.

TABLE 1.—*Variations in viscosity of starch with different concentrations and on different days*

Amount of starch used	Viscosity determined on—					Mean	Standard deviation [1] expressed as—		
	July 1	July 3	July 22	July 23	July 31		Centipoises	Grams, starch	Per cent, starch
Grams	*Centipoises*	*Centipoises*	*Centipoises*	*Centipoises*	*Centipoises*	*Centipoises*			
CANNA SAMPLE NO. 5 (LOW VISCOSITY)									
1.4	10.5	11.0	10 0	13.5	10.5	11.1	1.24	0.06	4.3
1.6	16 0	17.5	17.5	16.0	15.5	16.5	.84	.02	1.3
1.8	27.0	32.5	29.5	28.5	26.0	28.7	2.25	.02	1.1
2.0	47.0	57.0	59.5	52.0	52.0	53.5	4.36	.03	1.5
2.2	86.0	---	90.0	91.5	84.0	87.9	3.01	.02	.9
CANNA SAMPLE NO. 52 (HIGH VISCOSITY)									
1.2	11.5	12.5	12.5	12.0	---	12.1	0.42	0.01	0.8
1.4	20.0	23.0	21.0	22.0	24.0	22.0	1.41	.02	1.4
1.6	40 5	38.0	37.5	44.5	47.5	41.6	3.85	.03	1.9
1.7	51.0	57 0	59 0	60.0	66.5	58.7	5.00	.02	1.2
1.8	76.0	81.0	77.5	83.0	90.5	81.6	5.09	.02	1.1
POTATO SAMPLE NO. 14 (MEDIUM VISCOSITY)									
1 2	11.5	8.0	13.0	12.0	---	11.1	1.88	0 05	4.2
1.4	20.0	19.0	19.0	20.0	18.0	19.2	.75	.02	1 4
1.6	35.0	33.5	30.0	31.0	32 0	32.3	1 78	.02	1.3
1.8	57.0	53.5	59 0	52.0	51.0	54.5	3.03	.01	.6
1.9	82.0	69.5	70.0	64.5	---	71.3	6.42	03	1 6
2 0	95.0	89.0	---	---	85.5	89.8	3.92	.02	1.0
POTATO SAMPLE NO. 56 (HIGH VISCOSITY)									
0.9	12.5	13.0	---	11.5	---	12.3	0.62	0.02	2.2
1.0	14.5	19.0	---	16.5	17.0	16.8	1.60	.02	2.0
1.1	21.0	27.0	---	22.0	22.0	23.0	2.35	.03	2.7
1.2	29.0	36.5	30.5	28.0	33.0	31.4	3.06	.03	2.5
1.3	37.0	41.5	41.0	36.0	40.0	39.1	2.20	.02	1.5
1.4	52.0	58.0	---	48.0	52.0	52.5	3.57	.02	1.4
1.5	69.0	---	76.0	---	70.0	71.7	3.76	.01	.7

[1] The equation for the standard deviation is $\sqrt{\frac{\Sigma(x)^2}{n}}$, x being deviation from the mean and n, the number.

The values for standard deviation, expressed as grams of starch, were obtained by referring the centipoises of standard deviation to the point on the curve (fig. 1), which corresponds to the concentration of the starch used. The plus or minus deviation in grams of starch necessary to produce the standard deviation was then estimated. Values can not be determined accurately from a curve of this type, but they help to form an idea of the magnitude of the error involved. Table 1 shows that whereas the actual deviation from the mean value was considerable, the percentage of deviation was not large, particularly with the higher concentrations. In general, the percentage error decreased with concentration. The mean values given in Table 1 are plotted in Figures 1 and 2. In Figure 2, where the viscosity

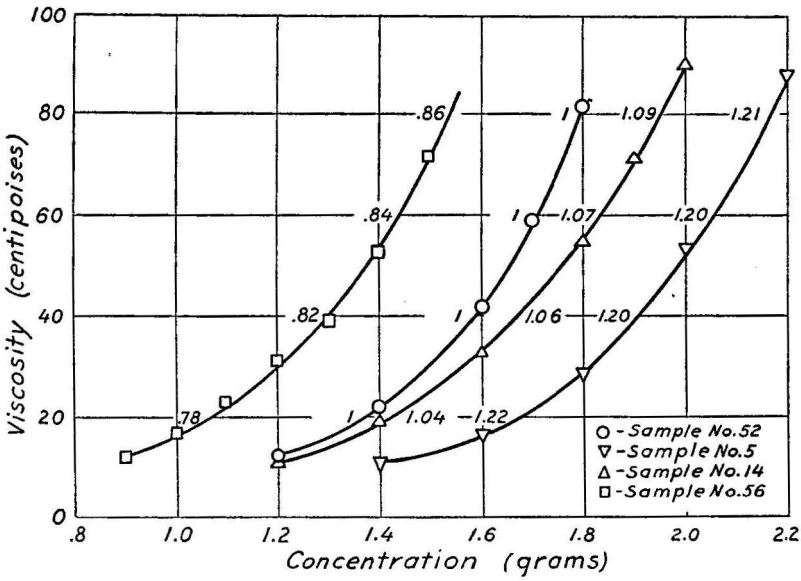

FIGURE 1.—Relation of viscosity and concentration

is plotted on the logarithmic scale, the graph is a straight line. This is similar to the results obtained by Rask and Alsberg (*15*).

Farrow and Lowe (*3*) point out that the apparent viscosity of a starch paste is dependent upon the pressure employed to produce the flow, viscosity decreasing with increasing pressure. This also was found to be true of results obtained with a rotating viscosimeter, the apparent viscosity varying with the rate of rotation. Rask and Alsberg (*15*) were able to obtain concordant results with wheat starch using different weights on the Stormer viscosimeter. Samec (*17, p. 257*) points out that below a certain upper pressure limit starch solutions do not obey Poiseuille's law, which states that the rate of flow of starch through a capillary tube is proportional to the pressure. Above this limit starches tend to obey the law. Soluble starch, he continues, obeys Poiseuille's law throughout. In the present investigation very different apparent viscosities were produced by changing the weight on the viscosimeter. A constant weight was therefore used throughout the experiment.

SWELLING POWER

It is well known that, when concentration is not too great, the swollen granules of an untreated starch—that is, a starch whose granules have not been ruptured by chemicals or by grinding—will settle, leaving a clear supernatant liquid. Harrison (*5, p. 87*) was among the first to correlate this swelling power with the strength of the starch paste. According to his method, a 1 per cent starch solution is prepared by heating on a water bath "to a few degrees above the temperature of swelling with careful mixing but not shaking." Fifteen cubic centimeters of the solution when cooled are poured into a graduated tube and centrifuged, and the volume of the settled starch granules is then read.

Katz (*10*) noted differences in the swelling power of wheat starch from fresh and from stale bread, the latter being about 60 per cent of

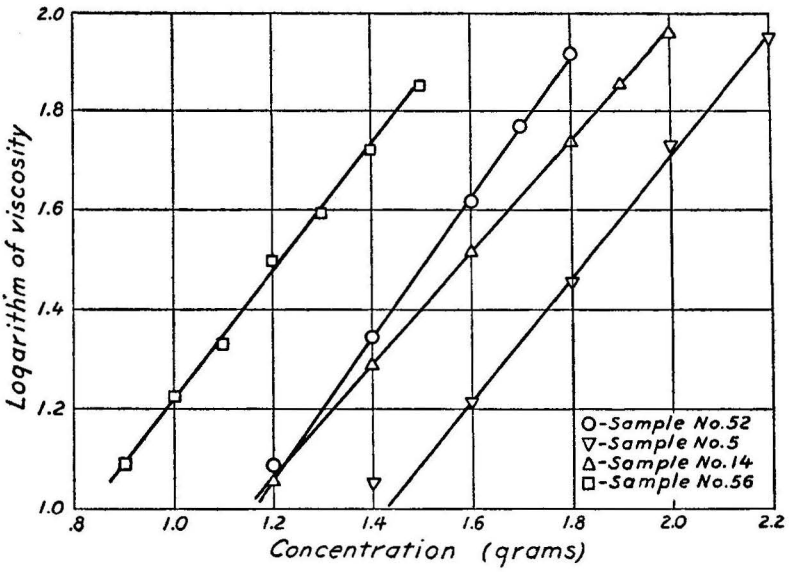

FIGURE 2.—Relation of logarithm of viscosity to concentration

the former. In this work the bread crumb was worked up with water and then passed through fine bolting cloth, and the volume of the settled starch was measured. Katz also studied the swelling power of pure starches using the same method of measurement. Since in bread making the starch swells with restricted amounts of water, he studied the swelling power of air-dried starch—that is, with no water added—and of starch to which different amounts of water up to 2,000 per cent (5 grams of starch in 100 cubic centimeters of water) had been added. He found that the swelling power increased rapidly with increasing amounts of water.

The method as used by Harrison (*5*) has the objectionable feature that the swell of the starch "just above its gelatinization point" is a measure of its swell at higher temperatures. Differences in starches which would be very appreciable at points of greater swell could be

easily obscured at the low temperatures used. It also requires a very low concentration of starch, especially when potato or canna starch is used. Regardless of the method of measurement used, it was found necessary to exercise great care with regard to temperature, time of cooking, and mechanical agitation, in preparing the solution.

METHOD OF DETERMINING SWELLING POWER

The following method for determining the swelling power was used in this study: The starch solution was prepared as previously described. It was cooked and poured into approximately 200 cubic centimeters of distilled water in a ring-necked cylinder. The flask in which the solution had been prepared was rinsed once with a little water which was added to the contents of the cylinder. The cylinder was tightly stoppered and slowly inverted twice to mix the contents gradually. The stopper was then removed, and the cylinder was allowed to stand undisturbed overnight. The following morning the volume of the settled granules was measured. Graduations on the side of the cylinder may be used for making the measurements, or a strip of paper wrapped around the cylinder and held in place by a rubber band, with the edge fitted exactly even with the top level of the starch granules, will answer the purpose. The volume may then be exactly determined by discarding the starch solution, filling the cylinder with water to the paper level, and measuring the volume of water. Usually the top boundary of the starch mass is very sharply defined, and the volume can be estimated to an accuracy of 1 cubic centimeter. The cylinders need not be of any exact dimension. Those used in this work averaged 5 centimeters in diameter and 25 centimeters in depth, and had a capacity of 400 cubic centimeters. The swell was expressed simply as cubic centimeters of swollen granules. The swelling power of a starch is defined as the volume in cubic centimeters of swollen granules of 1 gram of air-dried starch obtained by using the standard procedure.[4] With this method 60 determinations can be made in a day.

Figure 3 gives the swell-concentration curve of canna samples Nos. 5 and 52, and of potato samples Nos. 14 and 56. It will be noted that the swell is not quite a linear function, the curves bending somewhat toward the concentration axis. This may have been caused by decreased imbibition due to the increasing weight of the swollen granules with greater concentrations. Katz (*10*) found that with limited amounts of water the swelling power decreased as the concentration increased. This effect may be apparent even in the relatively low concentrations used here. As was pointed out in connection with the determination of viscosity, a series of closely agreeing results may be secured one day and a different series the next. Table 2 illustrates this fact.

[4] Air-dried starch suffices fully as well as a basis for computation as does oven-dried starch, since the potato and the canna starches have very nearly the same moisture content, which remains nearly constant at about 18 per cent.

TABLE 2.—*Variations in swell of canna sample No. 52 determined on successive days*

[Results expressed as cubic centimeter swell of 1.2 grams of starch by the standard procedure]

Test No.	Swell determined on—					
	Mar. 22	Mar. 23	Mar. 24	Mar. 25	Mar. 26	Mar. 30
	Cubic centimeters	*Cubic centimeters*	*Cubic centimeters*	*Cubic centimeters*	*Cubic centimeters*	*Cubic centimeters*
1	137.0	133.0	136.0	139.0	135.0	137.0
2	137.0	137.0	136.0	138.0	141.0	143.0
3	136.0	133.0	137.0	139.0	139.0	143.0
4	----	134.0	139.0	139.0	134.0	143.0
5	----	135.0	----	----	----	----
Average	136.6	134.4	137.0	138.7	137.2	141.5

The averages given in Table 2 have a mean of 137.7 cubic centimeters with a standard deviation of 2.15 cubic centimeters. Reference to the curve of canna sample No. 52 in Figure 3 shows that this is equivalent approximately to 2.1 per cent and 0.025 gram of starch.

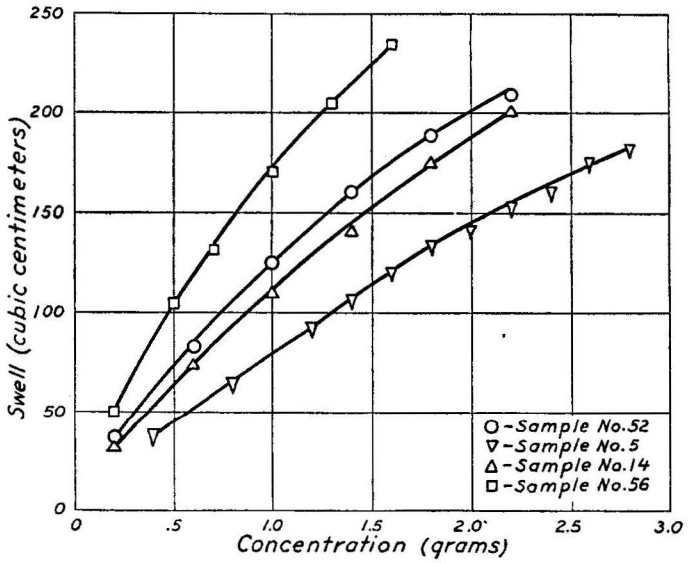

FIGURE 3.—Relation of swell to concentration

The swelling power was used as the method of measurement in a series of experiments conducted to determine the effect of variation in the procedure of preparing the starch solution.

EFFECT OF VARIATION IN PROCEDURE

A series of samples of 0.8 gram each were brought into solution by the standard procedure and placed in the cooker. At intervals a sample of each of the four starches was removed and the swell was determined.

Figure 4 shows the effect of the length of time of cooking on swell. The swell in all cases gradually increased with the length of time of cooking. After 15 minutes the curves level off to very slight increments for additional periods of cooking.

A series of 0.8-gram samples were brought into solution by the standard procedure and one sample each of the four starches was cooked for one hour, during which process the temperature of cooking was varied for the different samples. Figure 5 shows the effect of temperature of cooking on swell.

At the lower temperatures the four starches showed the same relationship previously noted in viscosity and swell. However, at the higher temperatures canna sample No. 52 fell below potato sample No. 14, and at boiling temperatures no settling was apparent except

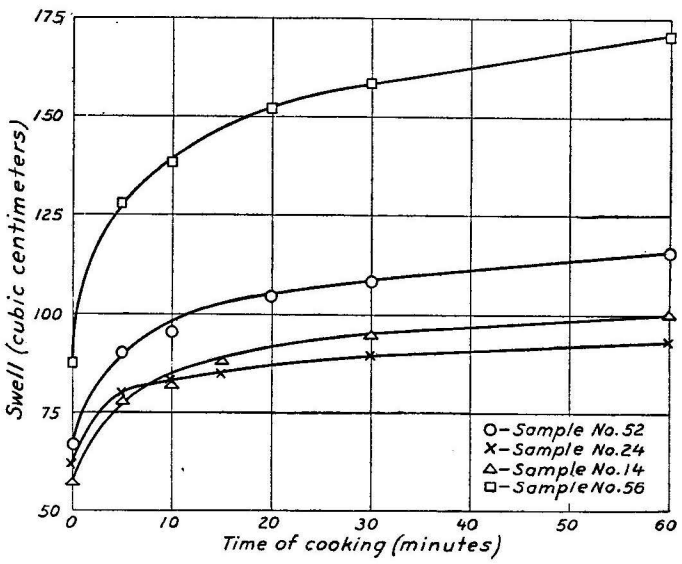

FIGURE 4.—Effect of time of cooking on swell. Temperature 80° C.

for a dense layer a few cubic centimeters in volume at the bottom. Examination of floating fragments of granules in the liquid after it had settled overnight showed that practically all the granules had burst, the layer at the bottom being the denser parts of the starch granule or the amylopectin. Potato sample No. 56 was affected in the same way by boiling. Potato sample No. 14 and canna sample No. 5, starches of low viscosity, showed no such effects. This demonstrates the greater stability of the starches of lower viscosity.

To determine the amount of swell of the various starches without cooking and to learn whether the swell would be affected by the length of time the starch solution stood before it was poured into the cylinders, a series of starch samples, 0.8 gram each, were brought into solution by the standard procedure and allowed to stand for varying lengths of time at room temperature. They were then poured into the cylinders as in the standard procedure. One sample thus prepared of each of the four starches was allowed to stand overnight before it was poured into the cylinder, and the swell was determined

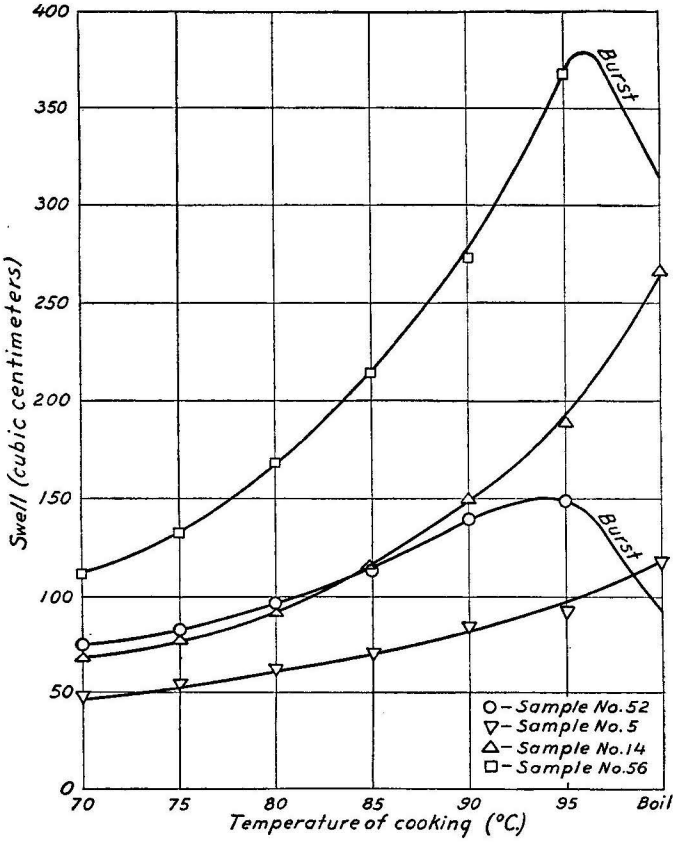

FIGURE 5.—Effect of temperature of cooking on swell. Time of cooking one hour

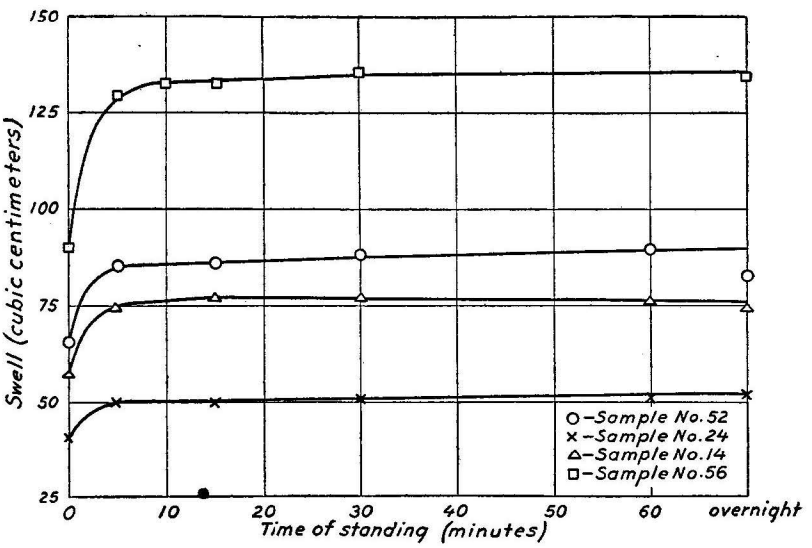

FIGURE 6.—Effect of time of standing on swell. No cooking

in the regular way. Figure 6 gives the results. Evidently the swell of all the starches increased rapidly for the first five minutes, and thereafter remained practically constant, even with the samples that stood overnight.

This fact makes it possible to determine the swell of starches without the use of a cooker and reduces the method to a procedure requiring only simple apparatus. It is only necessary to bring the starch into solution, allow it to stand for 10 minutes or longer, and then determine the volume of the swollen granules.

To determine the effect of the temperature of hot water on swell, 0.8-gram samples of starch were weighed into the Erlenmeyer flasks and mixed with 5 cubic centimeters of cold water. The starch was

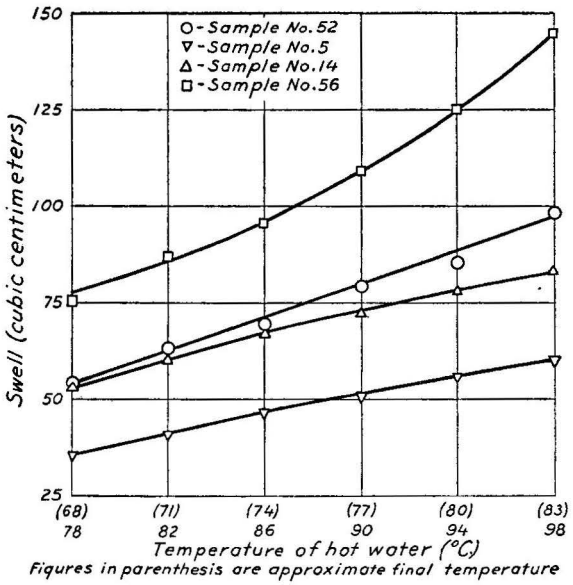

FIGURE 7.—Effect of temperature of hot water on swell

brought into solution by adding 100 cubic centimeters of hot water at varying temperatures. Instead of being cooked, the starch solution was allowed to stand for 15 minutes, and the swell was determined in the usual manner. Figure 7 shows a gradual increase in swell with increase in temperature of the hot water. The curve of the lower swelling starches bends somewhat toward the temperature axis, whereas that of potato sample No. 56 of high viscosity tends away from it.

To determine the effect of varying the amount of cold water and the temperature of the hot water used, with the final temperature remaining constant, solution of the starch was made in the regular manner, except that to part of the samples 2 cubic centimeters and 5 cubic centimeters of cold water were added instead of the 10 cubic centimeters usually used. One hundred cubic centimeters of hot water was added in each instance, but the temperature was varied so that it finally became the same, 80° C., for all. Table 3 gives the results.

TABLE 3.—*Effect on the swell of canna starch of varying the amount of cold water and the temperature of the hot water, with the final temperature remaining constant (80° C.)*

Canna sample No. 52	Swell of starch granules in—		
	10 c. c. of cold water (hot water at 97° C.)	5 c. c. of cold water (hot water at 94° C.)	2 c. c. of cold water (hot water at 92° C.)
Grams	*Cubic centimeters*	*Cubic centimeters*	*Cubic centimeters*
0.6	68	68	69
.8	88	87	89
1.0	105	109	105
1.2	122	121	119

Table 3 shows that the final temperature was the determining factor in the swelling method. Ordinarily 10 cubic centimeters of cold water was used in the standard procedure because it permits better dispersion of the starch and lessens its tendency to form lumps at the higher concentrations.

RELATION OF SWELLING POWER TO VISCOSITY

Harrison (*5, p. 87*) used the formula of Hatschek for computing the viscosity of a dispersoid from the volume of the dispersed solid. Thus, $\text{viscosity} = 1 + \left(4.5 \times \frac{\text{Volume of dispersed solid}}{\text{Total volume of solution}}\right)$. He found that the viscosity values checked very closely with the actual values determined by means of an Ostwald viscosimeter. He states, however, that this formula does not apply when the volume of the dispersed solid approaches 74 per cent of the total volume, "in which case the particles touch one another." In this work, Harrison heated the starches to slightly above their gelatinizing temperature. It is possible to consider the swollen starch granules in solution as dispersed solids if they have been subjected to only a small swell, particularly as in case of the small-grained cereal starches. However, this would hardly apply in the case of granules that are swelled at the higher temperatures and assume macroscopic dimensions, as with the large-grained tuber starches.

Reference to Figure 3 shows that when a sufficient concentration of starch is used the granules continue to imbibe water and to swell after they are poured into the cylinders. This occurs whether the starch solution is poured at once into the cylinder or is allowed to stand overnight in the flask (fig. 6), and there is little difference between the swelling power as determined in low concentrations and in high concentrations. These facts show that starch granules when heated in any given way have a definite capacity to swell. In a dilute solution with a swell of less than 110 cubic centimeters, the starch granules are saturated with water. In this condition they are rounded or spherical in shape and are capable of moving more or less freely.

When concentration of the starch is such that the swelling power exceeds 110 cubic centimeters the granules become unsaturated with water. This unsaturation should mean that the granules tend to approach 100 per cent of the volume of the solution. They would

thus fill all the interstices and become more or less distorted in shape. Where the degree of unsaturation is slight the granules are very flexible and probably slip by one another readily. Increasing the degree of unsaturation probably causes the granules to hold together more tightly. They then lose their ability to slip by one another, are reduced to flexibility, and the mass probably assumes a structural nature somewhat like that of lyophilic colloids, such as gelatin and agar-agar. This concept of a starch solution is true only when the proportion of whole to broken granules is sufficient to maintain the above-mentioned structure.

To determine the relationship between swell and viscosity, the values for the different concentrations of the four starches were taken

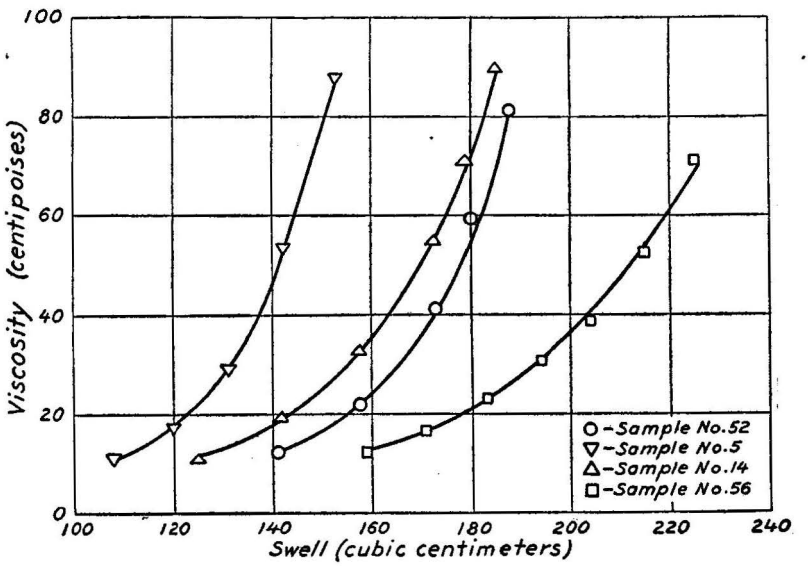

FIGURE 8.—Relation of viscosity and swell

from Figures 1 and 3 and plotted in Figure 8. It will be noted that the order of the starches has reversed itself from that of the concentration-viscosity curves (fig. 1), canna sample No. 5, low in viscosity, giving the greatest viscosity for a given swell, and potato sample No. 56, high in viscosity, giving the least. When viscosity is plotted on logarithmic scale the swell curves become straight lines as with the concentration curves. (Fig. 9.)

Obviously the swell of starches can not be used as a direct measure of viscosity, since if this were so the viscosity-swell curves of all the starches would coincide. If, however, the product of the concentration and swell is plotted against the viscosity, the values of the four starches arrange themselves as in Figure 10. These data are given in Table 4.

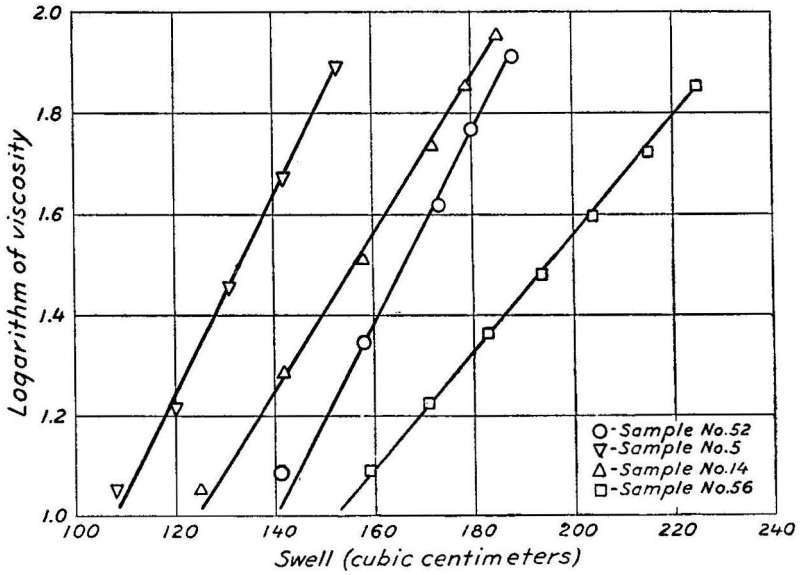

FIGURE 9.—Relation of logarithm of viscosity to swell

TABLE 4.—*Relation of concentration, swell, viscosity, and the product (concentration × swell)*

Canna sample No. 5 (low viscosity)				Potato sample No. 14 (medium viscosity)			
Concentration of starch	Swell	Concentration × swell	Viscosity	Concentration of starch	Swell	Concentration × swell	Viscosity
Grams	*Cubic centimeters*		*Centipoises*	*Grams*	*Cubic centimeters*		*Centipoises*
1.4	108	151	11.1	1.2	125	150	11.1
1.6	120	192	16.5	1.4	142	199	19.2
1.8	131	236	28.7	1.6	158	253	32.3
2.0	142	284	53.5	1.8	172	309	54.5
2.2	153	337	87.9	1.9	179	340	71.3
				2.0	185	370	89.8
Canna sample No. 52 (high viscosity)				Potato sample No. 56 (high viscosity)			
1.2	141	169	12.1	0.9	159	143	12.3
1.4	158	221	22.0	1.0	171	171	16.8
1.6	173	277	41.6	1.1	183	201	23.0
1.7	180	306	58.7	1.2	194	233	31.4
1.8	188	338	81.6	1.3	204	265	39.1
				1.4	215	301	52.5
				1.5	225	338	71.7

The curve, drawn through the averages of these points, becomes a straight line if the viscosities are plotted logarithmically, the equation being $y-0.45-0.00427\,x=0$, y being the logarithm of the viscosity in centipoises and x the product (concentration × swell). By means of this relationship it is thus possible, by determining the swell at any concentration, to substitute in the equation and solve for y the viscosity.

How accurately this relationship would apply to a wide variety of starches was not determined. It will be noted that the values of the four starches did not coincide. Particularly was this true of canna

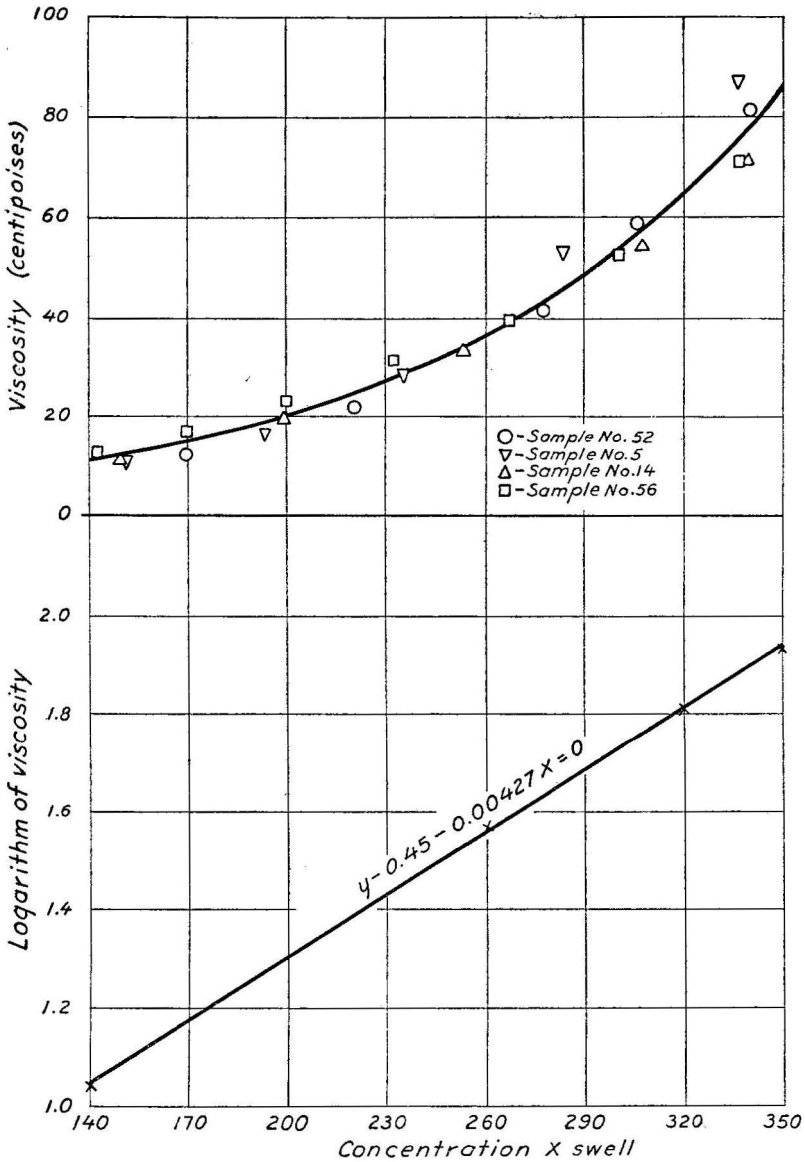

FIGURE 10.—Relation of the product (concentration × swell) to the viscosity and logarithm of viscosity

sample No. 5. The nearer the values were to the central part of the curve, the closer did the several starches approach the curve. These starches represent fairly wide variations in properties. Probably the values of most of the starches lie closer to the curve than do the

extremes noted above. Since the viscosity values are only relative, being dependent upon the weight used on the viscosimeter, the equation is not an absolute relationship but should be worked out for the particular procedure used.

EVALUATION OF THE STRENGTH OF A STARCH

Expression of the strength of a starch in absolute units of viscosity or swelling power is not a safe procedure, because of the differences in results caused by small changes in procedure, fluctuations in electrolyte content of the distilled water used, and the like. Results by these methods do have relative significance, however.

Wolff (*22, p. 1002*) has suggested that the relative strength of a starch is made more evident by referring the viscosity obtained to that of a standard starch. Under normal conditions of storage, air-dried starch is very stable in its physical properties and serves as a dependable standard. When a standard procedure for preparing the starch solution is used, the viscosity of a series of concentrations is determined on the standard starch and the plotted values are joined in a continuous curve. A viscosity determination at one concentration is made to determine the relative strength of an unknown starch. Dividing this concentration into the concentration of the standard starch required to give the same viscosity shows the relative strength. This method of calculation is based on the assumption that the ratio of the viscosity of the unknown to the standard starch is the same regardless of concentration. That this is not strictly true is evident from Figure 1 (p. 8), in which the ratios of the different starches, compared with canna sample No. 52 as unity, are given at different points on the curve. Within the same species the curves are proportional. Canna sample No. 5 is closely proportional to canna sample No. 52, whereas if potato samples Nos. 56 and 14 are expressed in terms of each other they become nearly proportional, particularly in the higher concentrations.

An obvious objection to the use of a standard starch is that the same starch would not be always used, and the results would not, therefore, be comparable. This fact need not affect the usefulness of such a starch for practical purposes, however. Any starch that has been found by actual factory test to be satisfactory may serve as a standard. The deviations of the starch under test from the standard can then be estimated in terms of the standard.

In Figure 1 the concentration curve of any of the four starches given might serve as a standard curve. For example, let it be assumed that canna sample No. 52 is the standard starch, and that 1.6 grams of the unknown sample has a viscosity of 24 centipoises. Reference to the standard curve shows that 1.43 grams of sample No. 52 is required to give this viscosity. Calculating the strength of the unknown, $1.43/1.6 \times 100$ equals 89 per cent, the standard (52) being 100 per cent. However, since some factor in the procedure may have caused the values for the standard to decrease from, or increase over, the values obtained when the standard curve was constructed, viscosity determination of canna sample No. 52 should also be made. If it be assumed that 1.6 grams of this sample has a viscosity of 44 centipoises, which is equivalent to 1.62 grams on the standard curve, the corrected value of the starch will be found to equal $1.43/1.62 \times 100$, or 88 per cent.

The curve in Figure 10 is used in evaluating a starch by means of its swell. Assuming that 1.5 grams of an unknown starch gives a swell of 155 cubic centimeters, the equation becomes $1.5 \times 155 \times 100$, or 233 (concentration × swell). The swell of 1.5 grams of canna sample No. 52, the standard starch, was 168 cubic centimeters, which equals 252 (concentration × swell). These values referred to the curve give 28 centipoises for the unknown, and 33 centipoises for the standard starches, which are equivalent to 1.48 and 1.53 grams, respectively, on the standard curve. Thus, the equation becomes $1.48/1.53 \times 100$, or 97 per cent, which is the relative value of the unknown starch.

Of the two methods of measuring viscosity, namely, the direct viscosity determination and the indirect determination of the viscosity from the swell, the former is undoubtedly the more nearly accurate, since the relationship of the product (concentration × swell) to viscosity is not absolute. The swelling method, however, has advantages, particularly for practical work. As has been stated, the method can be carried on rapidly and with simple apparatus by omitting the cooking of the starch.

EFFECT OF ELECTROLYTES ON SWELL AND VISCOSITY

That swell and viscosity of many emulsoid colloids are affected by small additions of electrolytes is well known. When neutral salts, for example, are used as the electrolyte the decrease in viscosity is relatively large with the first addition of the salts. Subsequent additions cause only a gradual decrease. Kruyt and De Jong (*11*) attribute the initial large decrease of viscosity to a discharge phenomenon based on the electro-viscous effect, and the subsequent gradual decrease to a lyotropic effect on hydration of the particles. De Jong (*9*), using a soluble starch, was able to show that the nature and the valency of the cation of the salts largely determine the effect, and that those of the anion have little effect. When cations up to quadrivalent were used the depression in viscosity of the starch solution for equivalent concentrations of the salts was the same for the cations of the same valency and increased with the valency. Gelatin and agar-agar show similar reactions with neutral salts. The three colloids differ with respect to acids and the alkalis. With agar-agar, hydrochloric acid and sodium hydroxide coincide in their effect with that of neutral salts. With gelatin, both acid and alkali occupy exceptional positions, whereas, with starch, only the alkali occupies an anomalous position, the acid having an effect similar to that of neutral salts. These differences may be explained by the fact that gelatin is amphoteric and assumes a plus or a minus residual charge, depending upon the reaction of the solution. Agar-agar does not function chemically either as an acid or as a base but resembles many other comparatively neutral substances in taking on a negative charge in colloidal solution. As will be discussed later, starch functions as an acid, hence the anomalous effect of sodium hydroxide.

Samec (*17, p. 272*), working with potato starch, found that with the addition of small amounts of alkali to the starch solution, the viscosity rose abruptly. Further additions caused a decrease in viscosity. With subsequent additions, viscosity again increased. This characteristic hump in the alkali viscosity curve was also found by De Jong (*9*), working with soluble starch and did not appear in the cal-

cium hydroxide ($Ca(OH)_2$) curve. This may be explained by the fact that final viscosity is the resultant of two opposite tendencies, namely, the swelling effect of the hydroxyl and the discharging effect of the cation. With calcium hydroxide the latter effect is greater than the former even in small concentrations.

EFFECT OF SODIUM CHLORIDE

Table 5 shows the effect of varying amounts of sodium chloride on viscosity and swelling power of two edible-canna and two potato starches.

TABLE 5.—*Effect of sodium chloride on viscosity and swell of edible-canna and potato starches*

Amount of 0.01 equivalent NaCl added	Canna sample No. 52 (high viscosity)		Canna sample No. 5 (low viscosity)		Potato sample No. 56 (high viscosity)		Potato sample No. 14 (low viscosity)	
	Viscosity	Swell	Viscosity	Swell	Viscosity	Swell	Viscosity	Swell
Cubic centimeters	*Centipoises*	*Cubic centimeters*	*Centipoises*	*Cubic centimeters*	*Centipoises*	*Cubic centimeters*	*Centipoises*	*Cubic centimeters*
0	89.0	178	32.0	117			54.0	159
.2	37.5	158				254		
.5			20.5	110	109.0	232		
1.0	21.0	149	16.5	108	93.0	225	37.0	151
2.0	14.0	128	12.0	102	65.0	200	27.0	144
3.0	11.5	120	11.0	98	41.0	186	22.5	138
4.0	9.5	113	9.0	94	32.0	177	18.0	135
6.0	8.5	104					14.5	127
10.0	6.0	95	7.0	86	16.5	142	14.0	124
[1] 40.0	4.5	73			7.5	101	8.0	96
100.0	4.0	66			6.0	88	7.0	87
400.0					6.0	80	9.0	82

[1] A solution of NaCl of equivalent strength instead of hundredth equivalent was used for these higher concentrations.

A 1.8-gram sample of starch was used in each instance. The electrolyte was added to the starch suspension before hot water was added in one-hundredth-equivalent solution. Corresponding amounts of cold water were subtracted so that 10 cubic centimeters was present in each instance. Otherwise the procedure as outlined previously (p. 5) was followed. Figure 11 shows graphically the effect of sodium chloride on viscosity and swell.

The above given data show very strikingly the same type of curve noted by Samec (*17*) and De Jong (*9*). The first additions of electrolyte produced a relatively great depression in both swell and viscosity. The effect of each succeeding addition was less. As has been stated, this decrease in viscosity, due to the presence of minute quantities of electrolyte, is attributed to the discharge of colloidal particles. De Jong (*9*) assumes that there would be no change in volume of the dispersed phase with small electrolyte concentrations, dehydration taking place only at much higher concentrations of salts. The fact that the volume of the swollen granules, as determined in the swelling method, does decrease greatly, due to the presence of electrolytes, may be perhaps ascribed to the "quasi-voluminous" effect, the theory being that if the particles are electrically

charged they surround themselves with a repellent sphere that increases their active volume. Alexander (*1*) states that with gelatin there is also a shrinkage in volume due to the addition of salts.

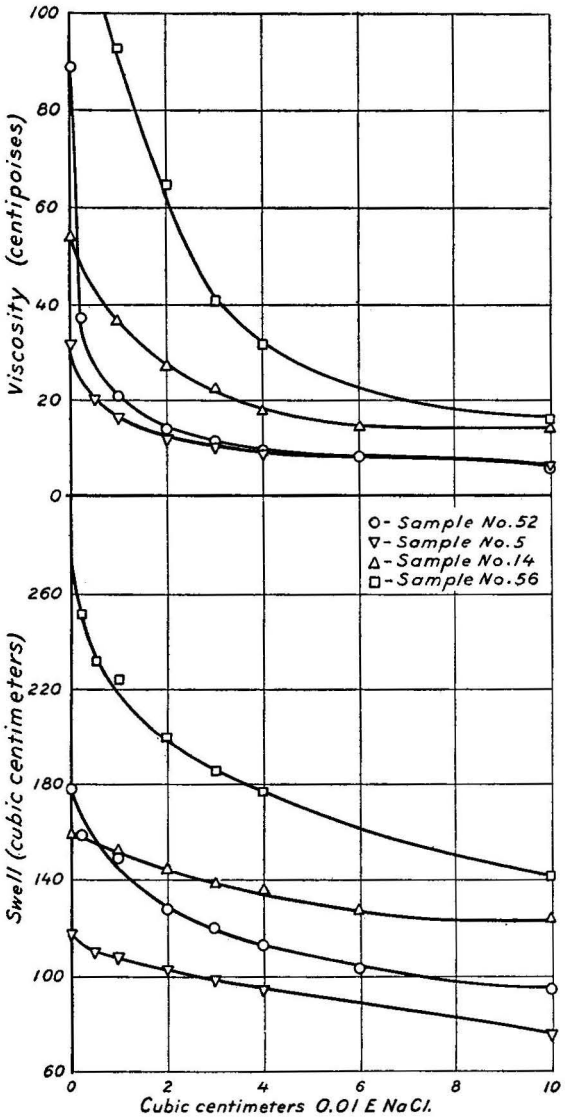

FIGURE 11.—Effect of sodium chloride on viscosity and swell

Electrostatic repulsion at the surface of the pores increases their size and the imbibition. Neutralization of these charges with electrolytes nullifies the charge and hence decreases the imbibition.

A marked difference is apparent in the relative effect of the sodium chloride on the four starches. Those of highest viscosity, potato

sample No. 56 and canna sample No. 52, were depressed to the greatest extent. Potato sample No. 14 and canna sample No. 5 were

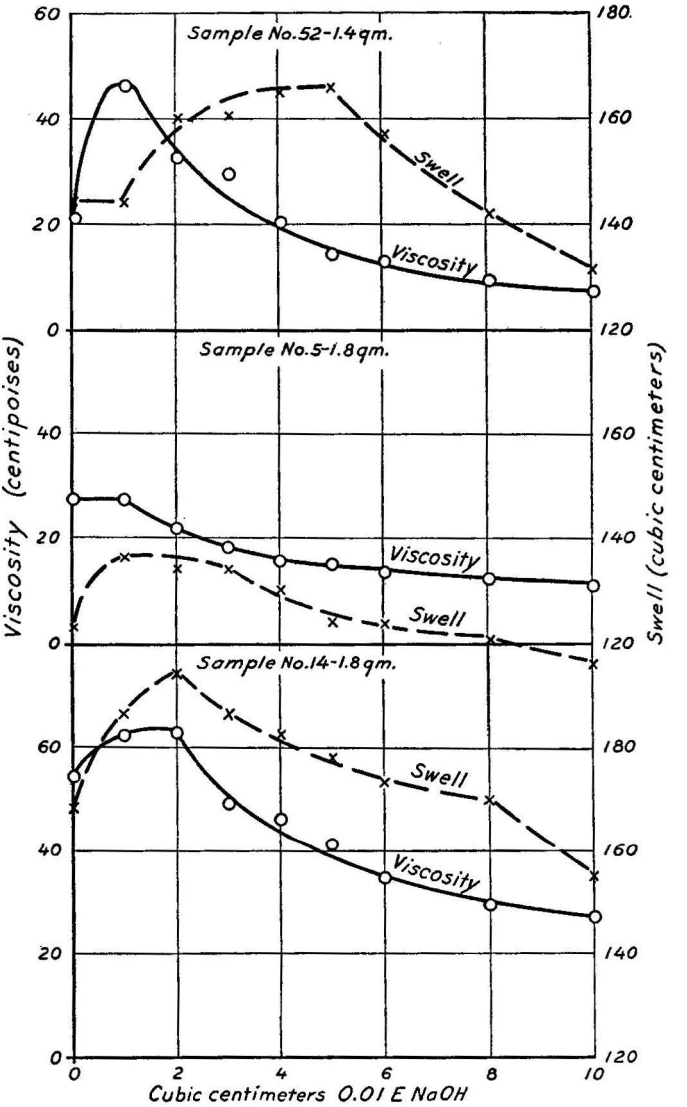

FIGURE 12.—Effect of sodium hydroxide on viscosity and swell

decidedly the more stable in this respect. The canna starch was affected to a greater extent than the potato starch.

EFFECT OF SODIUM HYDROXIDE

Table 6 and Figure 12 show the effect of varying amounts of sodium hydroxide (NaOH) on viscosity and swell.

TABLE 6.—*Effect of sodium hydroxide on viscosity and swell of edible-canna and potato starches*

Amount of 0.01 equivalent NaOH added	Canna sample No. 52 (1.4 grams) (high viscosity)		Canna sample No. 5 (1.8 grams) (low viscosity)		Potato sample No. 14 (1.8 grams) (medium viscosity)	
	Viscosity	Swell	Viscosity	Swell	Viscosity	Swell
Cubic centimeters	*Centipoises*	*Cubic centimeters*	*Centipoises*	*Cubic centimeters*	*Centipoises*	*Cubic centimeters*
0	20.5	144	27.0	123	54.0	168
1	46.0	144	27.0	136	62.0	186
2	32.5	160	21.5	134	62.5	194
3	29.5	161	18.0	134	49.0	186
4	20.0	165	15.5	130	46.0	182
5	14.5	166	15.0	124	41.0	178
6	13.0	157	13.5	124	34.5	173
8	9.5	142	12.5	121	29.5	170
10	7.5	132	11.0	116	27.0	155

The same increase in viscosity with subsequent depression noted by other investigators is apparent here. There is no consistent relationship between swell and viscosity as affected by sodium hydroxide. In canna sample No. 52 the peak of the viscosity curve was reached at 1 cubic centimeter—an amount that produced no increase in swell. Further additions of sodium hydroxide increased swell and decreased viscosity, the maximum of the former not occurring until 4 cubic centimeters of hundredth-equivalent sodium hydroxide was reached. Canna sample No. 5 increased considerably in swell but did not increase in viscosity with sodium hydroxide. Potato sample No. 14 showed a rough parallelism between swell and viscosity. These data strongly support the belief that other factors in addition to swell play a rôle in the viscosity of starch, particularly when electrolytes are concerned.

DEPRESSION IN SWELL BY EQUIVALENT AMOUNTS OF DIFFERENT ELECTROLYTES

Since starch is a negatively charged colloid, the nature and valency of the cation should have a decided effect on viscosity, whereas those of the anion should have little effect. To determine the effect of various electrolytes on swell, a series of salts were made up of hundredth-equivalent strength. In the present instance the procedure was somewhat different from that used previously. Uncooked starch was brought into solution and poured into the cylinder after being allowed to stand for 15 minutes. The electrolyte was added to the distilled water in the cylinder instead of to the raw starch in the flask. Varying amounts of the different salts were used, but since their effect can be shown as well by one concentration as by a series only the depression in swell, due to 2 cubic centimeters of different electrolytes, is given in Table 7.

TABLE 7.—*Decrease in swell due to 2 cubic centimeters of hundredth-equivalent electrolytes* [1]

Acids		Salts					
		Monovalent cations		Divalent cations		Trivalent cations	
Kind	Decrease in swell	Kind	Decrease in swell	Kind	Decrease in swell	Kind	Decrease in swell
	Cubic centimeters		*Cubic centimeters*		*Cubic centimeters*		*Cubic centimeters*
HCl	20	NaCl	19	$CaCl_2$	29	$Al_2(SO_4)_3$	68
H_2SO_4	20	NH_4Cl	18	$BaCl_2$	33	$FeCl_3$	20
H_3PO_4	16	KCl	18	$MgSO_4$	30		
Tartaric	21	KNO_3	18	$CuSO_4$	30		
		K_2SO_4	20	$ZnSO_4$	34		
		NaH_2PO_4	16	$FeSO_4$	37		
		Na_2HPO_4	9	$HgCl_2$	11		

[1] A 1.2-gram sample of canna starch No. 52 with a swell of about 115 cubic centimeters was used in all determinations.

Table 7 brings out strikingly the effect of the different groups of electrolytes. With certain exceptions there was excellent agreement among electrolytes of the same group, particularly among the acids and the salts of the alkali and the alkaline earth metals. The strong effect of the valency of the cation is evident. The effect of hydrogen as a cation was slightly greater than, but of the same order of magnitude as, the monovalent cations of the chloride, the sulphate, and the nitrate salts. The divalent alkaline earths caused a depression of one and one-half times, whereas the trivalent aluminum ion caused a depression of three and one-half times, that of the monovalent cations. With the exception of the phosphate ion, the anion appeared to have little effect. These data agree fairly well with results obtained by Kruyt and De Jong (*11*) working with agar-agar, and by De Jong (*9*) working with soluble starch.

Certain of the electrolytes did not produce a depression corresponding to their valency. Phosphoric acid, and the monosodium and disodium phosphates produced abnormally small depressions. This may be explained by the fact that the ionization of the third hydrogen of this acid is extremely small or may be attributed to the phosphoric acid which the starch molecule normally contains. The still smaller depression observed in the case of the disodium phosphate may have been due to the alkaline reaction of the salt. The small depression produced by the ferric chloride may have been due to the fact that, at the hydrogen-ion concentration of the starch solution, the iron was largely thrown out of solution, in which case the depression of 20 cubic centimeters would correspond exactly with that of an equivalent amount of hydrochloric acid. No explanation can be offered for the small effect of the mercuric chloride.

RELATIVE EFFECT OF THE HYDROXIDES OF SODIUM, CALCIUM, AND BARIUM

The procedure previously described (p. 21) was used to determine the effect on the swell of canna sample No. 52 of the hydroxides of sodium, calcium, and barium. Table 8 gives the results.

TABLE 8.—*Effect of different concentrations of the hydroxides of sodium, calcium, and barium on the swell of canna starch*

Amount of 0.01 N alkali used	NaOH		$Ca(OH)_2$		$Ba(OH)_2$	
	Swell	Gain (+) or loss (−) due to alkali	Swell	Gain (+) or loss (−) due to alkali	Swell	Gain (+) or loss (−) due to alkali
Cubic centimeters	*Cubic centimeters*	*Cubic centimeters*	*Cubic centimeters*	*Cubic centimeters*	*Cubic centimeters*	*Cubic centimeters*
0	115		115		115	
1	116	+1	105	−10	105	−10
2	118	+3	104	−11	106	−9
3	127	+12				
4	142	+27	94	−21	92	−23
5	141	+26				
6	136	+21	84	−31	81	−34
10	119	+4	75	−40	71	−44
[1] 20	104	−11				
40	98	−17				
80	97	−18				
120	100	−15				
160	104	−11				

[1] A solution of NaOH of normal strength instead of hundredth normal was used for these higher concentrations.

Table 8 shows that initial rise in the swell of the starch did not occur with calcium and barium hydroxides as with sodium hydroxide. Increasing the concentration of sodium hydroxide caused the swell to decrease to a minimum at about 80 cubic centimeters of hundredth-equivalent alkali. Beyond this there was a slight rise in swell. These data are in agreement with the results of Samec (*17, p. 272*) and De Jong (*9*) with viscosity measurements. The concentrations on the sodium hydroxide curve at the peak of the hump and the minimum value are of the same order of magnitude. Samec found that maximum viscosity at the hump occurred at 5×10^{-4}, and that minimum viscosity occurred at 1×10^{-3} normal. In Table 8 the 4 cubic centimeters of hundredth-equivalent sodium hydroxide which produced the maximum swell corresponded, when diluted to 300 cubic centimeters in the cylinder, to 1.3×10^{-4}, whereas the 40 cubic centimeters of hundredth-equivalent sodium hydroxide corresponded to 1.3×10^{-3}.

EFFECT OF REMOVING IONS BY DECANTATION

Since adsorption of electrolytes by emulsoids is a reversible reaction, it seemed probable that removal of the added electrolyte would result in an increase of swell of the starch. Two cylinders each of canna sample No. 52 and potato sample No. 14, in which the swell had been determined in the regular manner, were set aside for use. Electrolyte was then added to one sample of each starch. The other sample was left to serve as a check. Once every 24 hours the volume of the swollen granules was read from graduations on the side of the cylinder. The supernatant liquid was then carefully poured off, distilled water was added to make up the original volume, and the contents were carefully mixed. Table 9 shows the changes in swell due to successive decantations.

TABLE 9.—*Effect of repeated washings by decantation on the volume of swollen starch granules*

Treatment given	Length of time	Volume of swollen granules			
		Canna sample No. 52		Potato sample No. 14	
		No electrolyte	10 cubic centimeters 0.01-equivalent NaCl solution	No electrolyte	50 cubic centimeters 0.01-equivalent NaCl solution
	Days	*Cubic centimeters*	*Cubic centimeters*	*Cubic centimeters*	*Cubic centimeters*
Regular swelling method procedure	1	136	133	122	122
Electrolyte added, contents thoroughly mixed; stood 24 hours	2	(1)	83	(1)	83
Contents thoroughly mixed; stood 24 hours	3	135	83	123	85
Decanted supernatant liquid replaced an equal amount of distilled water and stood 24 hours	4	145	114	122	100
Do	5	162	143	120	129
Do	6	167	153	135	164
Do	7	149	159	173	198
Do	8	----------	159	----------	219
Do	9	----------	157	----------	235
Do	10	----------	----------	----------	233
Do	11	----------	----------	----------	267
Do	12	----------	----------	----------	262
Do	13	----------	----------	----------	225

[1] Since no electrolyte was added, the contents were allowed to stand undisturbed until the next day.

Before decantation was begun the nonelectrolyte or check samples were allowed to stand for 48 hours, when a second reading was taken. This reading was practically the same as the first. Similarly, the samples treated with electrolyte, after being allowed to stand for an additional 24 hours, showed nearly the same swell as in the first reading. This indicated the existence of a definite volume equilibrium between the granules and the solution.

Subsequent decantations caused an increase in swell. This was true of the check samples as well as those treated with the electrolyte. In the canna starch which was treated with 10 cubic centimeters of hundredth-equivalent sodium chloride, the swell increased practically to that in the check sample. The relatively large increase in the potato sample which was treated with 50 cubic centimeters of hundredth-equivalent sodium chloride suggests the possibility that the electrolyte may have produced in the starch granule a change not altogether physical. The large fluctuation in the results during the later decantations is indicative of the extreme sensitiveness of the swollen granules to minute changes in electrolyte content.

To learn whether any of the above-mentioned changes in swell were due to the breaking of granules, the soluble starch was determined in the supernatant liquid by the method of Rask (*14, p. 112*). A low concentration, 0.8 gram of canna sample No. 52, was used in order that there might be an increase in the proportion of liquid. Table 10 shows the soluble amylose in successive decantates. After the fifth decantate sodium chloride was added to the solution to determine whether sudden shrinkage caused any of the granules to break.

TABLE 10.—*Soluble amylose in successive decantates of distilled water and salt solutions from canna starch* [1]

Decantate No.	Volume of swollen grains	Weight of soluble amylose
	Cubic centimeters	*Grams*
1 (Distilled water)	87	0.0941
2 (Distilled water)	87	.0174
3 (Distilled water)	92	.0000
4 (Distilled water)	102	.0038
5 (Distilled water)	97	.0016
Total		.1169
6 (10 cubic centimeters of 0.01-equivalent NaCl added to distilled water)	45	.0026

[1] 0.8 grams of canna sample No. 52.

Table 10 shows that decantation and remixing of the starch granules with distilled water did not cause any appreciable breaking of the starch granules. Removal was practically complete after the second decantation. Sudden shrinkage from 97 to 45 cubic centimeters, due to the presence of electrolyte, did not result in any increase in soluble starch. The total soluble starch was 0.1169 gram or 14.6 per cent of the total weight of the starch.

EFFECT OF TREATING WITH MORE THAN ONE ELECTROLYTE

In order to gain further insight into the equilibrium between the swollen starch granule and the electrolytes, a series of blank swell experiments were made with canna sample No. 52 and potato sample No. 56 in which different combinations of electrolytes, as follows, were used:

Experiment 1.—Canna sample No. 52. Blank = 122 cubic centimeters.
Blank + 5 cubic centimeters 0.01-equivalent NaOH + 2 cubic centimeters 0.01-equivalent NaCl = 119 cubic centimeters.
Theoretical value:
Blank + 5 cubic centimeters 0.01-equivalent NaOH = 148 cubic centimeters = + 26 cubic centimeters.
Blank + 2 cubic centimeters 0.01-equivalent NaCl = 101 cubic centimeters $= \frac{-21 \text{ cubic centimeters}}{+5 \text{ cubic centimeters}}$.
122 cubic centimeters + 5 cubic centimeters = 127 cubic centimeters (as compared with 119 cubic centimeters found).

Experiment 2.—Blank + 1 cubic centimeter 0.01-equivalent HCl + 2 cubic centimeters 0.01-equivalent NaCl = 91 cubic centimeters.
Theoretical value:
Blank + 1 cubic centimeter 0.01-equivalent HCl = 111 cubic centimeters = − 11 cubic centimeters.
Blank + 2 cubic centimeters 0.01-equivalent NaCl = 101 cubic centimeters $= \frac{-21 \text{ cubic centimeters}}{-32 \text{ cubic centimeters}}$.
122 cubic centimeters − 32 cubic centimeters = 90 cubic centimeters (as compared with 91 cubic centimeters found).

Experiment 3.—Canna sample No. 52. Blank = 110 cubic centimeters.
Blank + 3 cubic centimeters 0.01-equivalent NaOH = 122 cubic centimeters (A).
A + 3 cubic centimeters 0.01-equivalent HCl = 91 cubic centimeters.
Theoretical value:
Blank + 3 cubic centimeters 0.01-equivalent NaCl = 93 cubic centimeters (as compared with 91 cubic centimeters found).

Experiment 4.—Potato sample No. 56. Blank = 159 cubic centimeters.
Blank + 3 cubic centimeters 0.01-equivalent NaOH = 182 cubic centimeters (A).
A + 3 cubic centimeters 0.01-equivalent HCl = 139 cubic centimeters.
Theoretical value:
Blank + 3 cubic centimeters 0.01-equivalent NaCl = 188 cubic centimeters (as compared with 139 cubic centimeters found).

In each of experiments 1, 2, and 3, a different set of conditions existed. In experiment 1 the sodium hydroxide tended to increase the swell and the sodium chloride to decrease it, and the resultant reaction of the two was alkaline. The theoretical value of 127 cubic centimeters is too great for the actual value of 119 cubic centimeters. In experiment 2 both electrolytes caused a decrease in swell, and the resultant reaction was acid. The theoretical value of 90 cubic centimeters agrees well with the actual value of 91 cubic centimeters. In experiments 3 and 4 the amount of hydrochloric acid used on the second day to neutralize the sodium hydroxide added gave a final value which was practically the same as for that of 3 cubic centimeters of sodium chloride. The disparity between the actual and the theoretical results in experiment 1 may well have been due to the abnormal behavior of the starches in an alkaline medium.

Results of these experiments show that the swollen granules of starch are in a state of definite equilibrium with the external solution. Where no electrolytes are added, as in the regular swell method, the volume of the swollen granules remains practically constant so long as the electrolyte content of the external solution is not changed. Decantation and replacement of the original solution with distilled water decreased the electrolytes and hence produced a new equilibrium point. The facts that when two electrolytes were added at the same time, the result was the algebraic sum of each, when added singly, and that when hydrochloric acid was added in equivalent quantities to the sodium hydroxide so as to produce sodium chloride the same result was obtained as if sodium chloride had been added, seem to offer conclusive proof that a true equilibrium was established and that it was reversible.

EFFECT OF SUBSTITUTING AND REMOVING ELECTROLYTES

OCCURRENCE OF ELECTROLYTES IN STARCHES

All natural starches have long been known to contain a certain amount of electrolytes that can not be removed by washing with water. Formerly they were considered to be adsorbed impurities. Later it was found that while the cations could be removed with comparative ease, phosphoric acid always remained and could not be removed except by the use of very drastic methods. Samec (*17, p. 18*) states that when a starch is washed with acid to remove the cations the phosphoric acid of the starch acts as a dibasic acid when titrated with alkali, with phenolphthalein and methyl orange as indicators. The fact that the phosphoric acid combines firmly with the starch and yet can be split off by hydrolysis when heated with water under pressure caused Samec to conclude that the acid exists as an amylophosphoric acid ester with one or two of its valencies satisfied by bases. He found that phosphoric acid exists very largely in the amylopectin. The fact that the amylopectin loses its viscous

nature when the phosphorus is removed and again becomes viscous when rephosphorized led Samec to believe that the existence of the phosphoric acid ester is alone responsible for the ability of starches to form viscous solutions.

Combination of amylophosphoric acid ester with different cations produces very decided differences. Walton (*21, p. 55*) describes the potassium salts as a viscous jelly, and the barium salts as only slightly soluble, forming cloudy and much less viscous pastes. Without cations the ester appears as a transparent jelly. Wolff (*22, p. 1002*) was able to substitute different cations in the natural potato starch by shaking the solution with neutral salts and then washing it with distilled water. If the viscosity of the normal starch was taken as 100 per cent, the sodium was 104, the potassium 102, the magnesium 93, and the calcium 91.5 per cent.

Samec states that the phosphoric acid ester is more or less completely neutralized in the storage organ of the plant by potassium, or by calcium or magnesium. In the potato it exists as the potassium acid salt although in the process of manufacture of the starch it is changed in part to the calcium salt by the calcium in the tap water. Tryller (*20*) made a complete ash analysis of a series of potato starches of different quality and which were given different treatments. He calculated the ratio of the bases to the phosphorus as equivalent bases for 1-gram atom of phosphorus. He found that in the natural starches the equivalent bases varied from 1.19 to 1.85. The starch with 1.19 base equivalent required 10 cubic centimeters of a tenth-normal sodium hydroxide solution to neutralize it. Equivalents of 1.54 required 1 cubic centimeter of a tenth-normal sodium hydroxide solution. Equivalents of 1.67 were neutral, and equivalents of 1.85 were alkaline. Treating with limewater resulted in 2.16 equivalents and washing with 1 per cent of hydrochloric acid left only 0.22 equivalents. The reaction and degree of saturation with bases thus constitute distinguishing differences between starches.

DETERMINATION OF THE HYDROGEN-ION CONCENTRATION OF STARCHES

The hydrogen-ion concentration is usually determined colorimetrically. Grimshaw (*4*) used a 10 per cent starch solution stirred in a mechanical stirrer for 15 minutes. The suspension was then centrifuged and the hydrogen-ion concentration of the clear liquid determined colorimetrically. In the present investigation the use of the colorimetric method often gave trouble. In certain starches the color of the indicator in the test solution sometimes changed rapidly when the solution was allowed to stand for a few minutes, probably because of adsorption by the soluble amylose in solution. The fact that a water extract of starch contains appreciable amounts of phosphates made it seem probable that there might be sufficient buffering to permit the use of electrometric methods.

An attempt was first made to use the water extract and the quinhydron electrode. This method was discarded, however, when duplicate determinations made on separate water extracts often were found to vary several tenths of a pH. This was caused by variation in the water extracts since duplicates on the same extract agreed closely. It was found that closely agreeing duplicates could be obtained by making the determinations in the starch suspension. Stirring must be rapid enough to keep all the starch in suspension.

This was accomplished by using an adjustable speed electric stirrer having a T-shaped rod. The starch was kept in suspension with the minimum of agitation. The hydrogen-ion concentration of the starch suspension was often two-tenths or three-tenths of a pH lower than that of the water extract. Considering the nature of the bonding of the phosphate ion to the starch granule, it seems probable that only a small part of the ion enters into the water extract. This part may or may not be in direct proportion to the amount of cation that goes into solution or to the amount that establishes equilibrium with the quinhydron in the starch suspension.

To determine the length of time they required to reach constant values, 1 to 5 starch-water suspensions were stirred with the quinhydron in the electrode, and the readings were taken from time to time. The

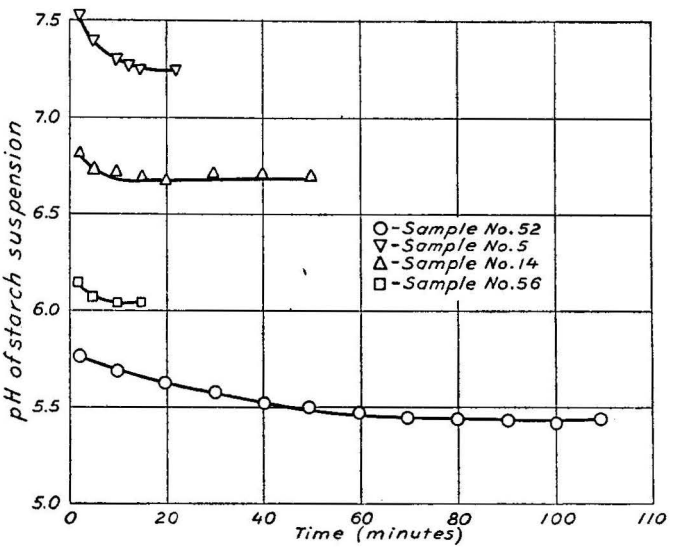

FIGURE 13.—Relation of time of stirring to hydrogen-ion concentration.

time hydrogen-ion concentration curves for four starches are shown in Figure 13. All the starches except canna sample No. 52 reached equilibrium within 10 to 15 minutes. With sample No. 52 there was a gradual decrease in pH and a constant value was reached only after 80 minutes of stirring.

Figure 14 shows the relation of hydrogen-ion concentration to starch-water ratio for canna sample No. 52 and for potato sample No. 14. The values in the curves represent the reading after a constant value had been reached. This graph shows that a 1 to 10 or even a 1 to 20 starch-water ratio may be used for hydrogen-ion determination. For the hydrogen-ion determinations given in subsequent tables, a starch-water ratio of 1 to 20 was used.

EFFECT OF THE VALENCE OF THE CATION

To determine the effect of varying the cations in canna starches as compared with potato starches, a series of starches were prepared from the natural starches, with salts with cations of different valency.

The following standard procedure was adopted: 50-gram samples of air-dried starches were shaken with 1,000 cubic centimeters of hundredth-equivalent electrolyte for 20 minutes. They were then allowed to stand from 20 to 60 minutes until settling was completed. The supernatant solution was then poured off, and fresh electrolyte

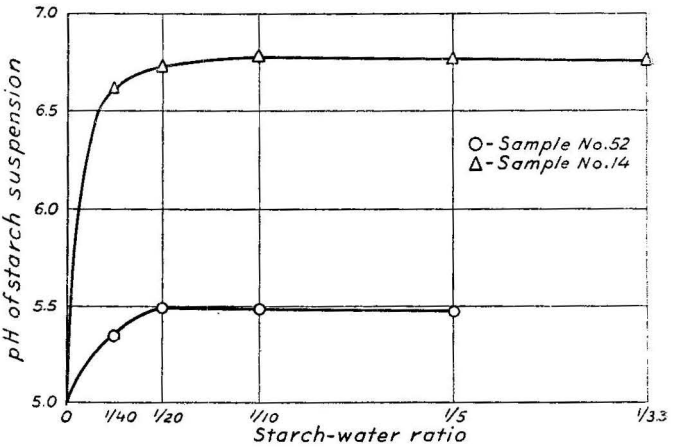

FIGURE 14.—Relation of starch-water ratio to hydrogen-ion concentration.

solution was added. This process was repeated three times. After receiving four treatments with electrolyte the starches were similarly treated with distilled water to wash out the excess of electrolyte. Three washings were found to be sufficient in most instances. The treated starches were dried in the same way as the original starches. Determinations were then made of the hydrogen-ion concentration, swell, viscosity, and reaction to electrolytes. Table 11 gives the results.

The swelling power was determined according to the standard procedure (p. 10) in 1 gram of air-dried starch that had been cooked for 15 minutes. The relative swell, as given in the table, is the swelling power divided by the swell of the original starch from which the treated starch was prepared. The relative viscosity with respect to the original starch was determined as previously outlined (p. 19). The change in swell due to electrolytes was determined on swell of the uncooked starch, as described on page 14, 1.2-gram samples of starch being used in all instances.

Table 11 shows the very striking effect of pretreating the raw starches with electrolytes. In each case the use of sodium chloride produced marked increases in swell and viscosity over those of the original starch, the increase in the two being practically the same. The increase was very large compared with that reported by Wolff (*22, p. 1002*) who found a maximum increase of 109, taking that of the original starch as 100. In Table 11 the least increase from sodium chloride in the case of canna sample No. 5 was 32 per cent for swell and 39 per cent for viscosity. In general potato sample No. 56 and canna sample No. 52, each of high viscosity, produced the greatest increases, whereas canna samples Nos. 24 and 5, each of low viscosity, produced the least, although the differences were not great. The use of potassium chloride gave results very similar to those with sodium

TABLE 11.—*Effect of the nature of the electrolyte on the properties of starches*

Laboratory No.	Nature of electrolyte added to raw starch	pH of raw starches	Swelling power	Relative swell (original starch as 100)	Relative viscosity (original starch as 100)	Change in swell due to electrolytes added to swollen starch (1.2-gram sample)						
						No electrolyte blank	NaCl 0.01 equivalent—2 cubic centimeters		$CaCl_2$ 0.01 equivalent—2 cubic centimeters		NaOH 0.01 equivalent—4 cubic centimeters	
							Change of swell	Ratio of residual swell to blank [1]	Change of swell	Ratio of residual swell to blank [1]	Change of swell	Ratio of residual swell to blank [1]
			Cubic centimeters			*Cubic centimeters*	*Cubic centimeters*	*Per cent*	*Cubic centimeters*	*Per cent*	*Cubic centimeters*	*Per cent*
CANNA STARCH												
52	None (original starch)	5.46	110	100	100	123	−21	83	−34	72	+17	114
52	NaCl 0.01-equivalent solution	5.23	166	151	148	181	−49	73	−80	56	−11	94
52	KCl 0.01-equivalent solution	5.60	163	148	150	180	−52	71	−76	58	−7	96
52	$CaCl_2$ 0.01-equivalent solution	6.06	86	78	82	89	−6	93	−14	84	+17	119
52	$BaCl_2$ 0.01-equivalent solution	5.69	86	78	84	91	−7	92	−19	79	+17	119
52	$Al_2(SO_4)_3$ 0.01-equivalent solution	4.40	40	36	45	42	+3	107	+3	107	+30	171
52	NaOH 0.01-equivalent solution	7.10	126	114	128	149	−29	81	−40	73	−7	95
52	HCl 0.002-equivalent solution	3.68	[2]		27	121						
24	None (original starch)	7.01	72	100	100	81	−4	95	−12	85	+3	104
24	NaCl 0.01-equivalent solution	6.98	104	144	149	119	−18	85	−32	73	+7	106
24	$CaCl_2$ 0.01-equivalent solution	6.78	69	95	96	73	−2	97	−4	94	+13	118
5	None (original starch)	7.28	72	100	100	76	−5	93	−14	82	+8	110
5	NaCl 0.01-equivalent solution		95	132	139	106			−30	72	+11	110
5	$CaCl_2$ 0.01-equivalent solution		62	86	89	69		100	−11	84	+12	117
5	NaOH 0.01-equivalent solution	7.49	84	117	116	90	−6	93	−14	84	+12	113
POTATO STARCH												
14	None (original starch)	6.76	100	100	100	124	−6	95	−14	89	+37	130
14	NaCl 0.01-equivalent solution		143	143	149	167	−23	86	−45	73	+10	100
14	$CaCl_2$ 0.01-equivalent solution	6.60	89	89	102	110	−8	93	−10	91	+22	192
56	None (original starch)	6.06	155	100	100	205	−29	86	−53	74	+49	124
56	NaCl 0.01-equivalent solution	6.41	260	168	158	257	−62	76	−92	64	−10	96
56	$CaCl_2$ 0.01-equivalent solution	6.42	122	79	88	159	−19	88	−27	83	+30	119

[1] This column expresses the swell of the sample, after the electrolyte has been added, in terms of per cent of the original or blank. For example, the swell of 52 after 2 cubic centimeters of NaCl had been added was 181−49=132, which is 73 per cent of that of the blank 181.

[2] Burst.

chloride. The use of calcium chloride caused a decrease in each instance. The difference in the relative decrease for the various starches was considerable. The least decrease was with canna sample No. 24, the swelling power dropping from 72 to 69, and the greatest decreases were with canna sample No. 52 and potato sample No. 56, the swell decreasing from 110 to 86 and from 155 to 122, respectively. There was excellent agreement between results with barium chloride and calcium chloride. The use of aluminum sulphate caused a great decrease in swell and viscosity of canna sample No. 52, the swell being only 36 per cent, and the viscosity 45 per cent, of the original. Treating with sodium hydroxide gave similar increases in swell and viscosity for samples Nos. 5 and 52. The use of hydrochloric acid, even of 0.002-normal strength, so weakened the granules that they burst on being cooked, and the viscosity was only 27 per cent of the original. Pretreatment of the raw starches with neutral salts of alkalis and alkaline earths produced variable effects on the hydrogen-ion concentration. The use of aluminum sulphate and of hydrochloric acid caused a pronounced lowering of pH, whereas the use of sodium hydroxide made the starches alkaline in each instance.

Comparison of the original and the treated starches shows that whenever the swell of the raw starch was increased by the pretreatment with sodium chloride and potassium chloride, the swell of the treated starches was decreased to a greater extent by the addition of sodium chloride and calcium chloride and increased to a lesser extent by the addition of sodium hydroxide than with the original. Where the swell was decreased, as with the calcium chloride and the barium chloride treatments, the opposite was true, the decrease due to the addition of sodium chloride and of calcium chloride being less than in the original and the increase due to the addition of sodium hydroxide usually greater. The decrease in swelling power of the starch treated with aluminum sulphate was so great that both sodium chloride and calcium chloride caused an increase in the swell, and the use of sodium hydroxide resulted in an abnormally large increase. Canna samples Nos. 52 and 5, which were treated with sodium hydroxide, showed no special abnormalities, and in general resembled the starches treated with monovalent salts. Again, relative differences appeared between the more viscous starches, potato sample No. 56 and canna sample No. 52, and the less viscous starches, canna samples Nos. 5 and 24, and potato sample No. 14. The latter are relatively the more stable, showing less increase in swell when treated with monovalent salts and less decrease when treated with bivalent salts. Likewise, in change in swell due to the presence of electrolytes, they showed less depression when treated with sodium chloride and with calcium chloride. In general starches of canna sample No. 52 and of potato sample No. 56 which were treated with calcium chloride resembled the original starches of canna samples Nos. 5 and 24 and of potato sample No. 14 in their properties.

In Table 11 two different phenomena produced by the same electrolyte are considered. In one instance the raw starch was treated with the electrolyte, and the excess was washed out; and in the other minute quantities of the electrolyte were added to the swollen starch. If the monovalent cations are considered, the effect in the two instances will be found to be diametrically opposite, the raw starch treated with sodium chloride increasing greatly in swell and the swollen starch treated with sodium chloride markedly decreasing.

The viscosity of starch solutions is considered by some investigators to be due to the capacity of the amylophosphoric acid ester to swell with the imbibition of water. Alterations in viscosity are considered to be due to alterations in the degree of ionization, the amylophosphoric anion being highly hydrated and the nonionized compound weakly hydrated. De Jong (*9*) regards the decreases in viscosity upon the addition of neutral salts in low concentrations to the cooked starch as a discharge phenomenon, the hydration remaining constant with small concentrations, and the phenomenon thus being purely physical.

The data in Table 11 show that the amount of depression in the swell due to treatment with electrolyte is dependent largely upon the swell and not upon the previous treatment given the raw starch. For example, the addition of 2 cubic centimeters of hundredth-equivalent sodium chloride to the swollen granules of a raw starch pretreated with sodium chloride, as in the case of canna sample No. 52, gave no abnormal decrease over other starches of similar swelling power but not treated with sodium chloride. Similarly, a raw starch treated with calcium chloride, as in the case of canna sample No. 52, made no abnormal decrease in swell due to the addition of calcium chloride to the swollen granules. The raw starches when pretreated with sodium hydroxide, as in the case of canna samples Nos. 52 and 5, showed no abnormal reactions in the swollen state to sodium hydroxide. These facts would seem to point further to the purely physical nature of the decrease in swell and viscosity due to small amounts of electrolytes. That treatment of the raw starch results in the more or less complete substitution of the cation of the electrolyte for that originally in the starch has been proved by actual analysis by Tryller (*20*). This fact and the fact that amylopectin prepared with different cations show very marked differences in swell seem to indicate that the chemical nature of the cation combined with the amylophosphoric acid is a strong determining factor in the swell and the viscosity of a starch.

EFFECT OF CONCENTRATION OF THE SALTS AND NUMBER OF TREATMENTS

Table 12 shows the effect of concentration and number of treatments.

TABLE 12.—*Effect of concentration of sodium chloride and number of treatments on the properties of starches*

Laboratory No.	Treatment of raw starch	pH of raw starches	Swelling power	Relative swell (original starch as 100)	Relative viscosity (original starch as 100)	Change in swell due to electrolytes added to swollen starch (1.2-gram sample)						
						No electrolyte blank	NaCl 0.01 equivalent—2 cubic centimeters		$NaCl_2$ 0.01 equivalent—2 cubic centimeters		NaOH 0.01 equivalent—4 cubic centimeters	
							Change of swell	Ratio of residual swell to blank [1]	Change of swell	Ratio of residual swell to blank [1]	Change of swell	Ratio of residual swell to blank [1]
			Cubic centimeters			*Cubic centimeters*	*Cubic centimeters*	*Per cent*	*Cubic centimeters*	*Per cent*	*Cubic centimeters*	*Per cent*
CONCENTRATION OF SODIUM CHLORIDE, CANNA STARCH												
52	None (original starch)	5.46	110	100	100	123	−21	83	−34	72	+17	114
52N–1	0.1×0.01-equivalent NaCl	5.69	122	111	110	131	−27	79	−47	64	+12	109
52N–2	0.5×0.01-equivalent NaCl	5.32	147	134	135	161	−43	73	−64	60	+3	102
52A	0.01-equivalent NaCl	5.23	166	151	148	181	−49	73	−80	56	−11	94
52N–3	5.0×0.01-equivalent NaCl	5.86	183	166	154	188	−56	70	−86	54	−11	94
52N–4	25.0×0.01-equivalent NaCl	5.49	171	155	152	179	−54	70	−81	55	−7	96
24	None (original starch)	7.01	72	65	100	81	−4	95	−12	85	+3	104
24A	0.01-equivalent NaCl	6.98	105	95	149	114	−17	85	−31	73	+7	106
24C	25.0×0.01-equivalent NaCl	7.34	131	119	182	148	−18	88	−37	75		
CONCENTRATION OF SODIUM CHLORIDE, POTATO STARCH												
14	None (original starch)	6.76	100	100	100	109	−6	95	−14	87	+37	134
14A	0.01-equivalent NaCl		143	143	149	149	−24	84	−40	73	+9	106
14C	25.0×0.01-equivalent NaCl	6.72	164	164	170	169	−30	82	−56	67	+14	108
NUMBER OF TREATMENTS, CANNA STARCH												
52	None (original starch)	5.46	110	100	100	123	−21	83	−34	72	+17	114
52M–1	1 treatment with 0.01-equivalent NaCl	6.35	117	107	111	124	−21	83	−30	76	+25	120
52M–2	2 treatments with 0.01-equivalent NaCl	6.23	128	117	123	138	−33	76	−51	63	+8	106
52A	4 treatments with 0.01-equivalent NaCl	5.23	166	151	148	181	−49	73	−80	56	−11	94

[1] See footnote 1 of Table 11.

Table 12 shows that increasing the strength of electrolyte up to 5×0.01-equivalent sodium chloride produces increasing swell and viscosity. A strength of 25×0.01-equivalent results in a slight decrease from 5×0.01 equivalent. The relation of the swelling power to change in swell due to the addition of electrolytes to the swollen starch is well brought out in the canna sample No. 52 series. In progressing from sample No. 52 to a strength of 5×0.01-equivalent sodium chloride in sample No. 52N–3, the depression of the swell due to the presence of sodium chloride and calcium chloride becomes increasingly greater, whereas an initial increase of 17 cubic centimeters in canna sample No. 52 due to the presence of sodium hydroxide changes to a decrease of 11 cubic centimeters in the 5×0.01-equivalent sample. The table also shows that swell and viscosity increase with the number of treatments given. These results show that replacement of the cations of the starch with those of the electrolyte takes place slowly. The data presented in Table 11 are thus only relative and do not represent pure sodium starches and pure calcium starches.

EFFECT OF SUCCESSIVE TREATMENTS WITH DISTILLED WATER AND WITH DIFFERENT CATIONS

Table 13 shows the effect of successively treating starch with distilled water and with different cations. In certain samples the starch granules burst during cooking. In such instances a similar uncooked sample was used to determine swell.

TABLE 13.—*Effect of successive treatments of canna starch with distilled water and with different electrolytes*

Laboratory No.	Starch sample used	Treatment	pH of raw starches	Swelling power	Relative swell (original starch as 100)	Relative viscosity (original starch as 100)	Swell of uncooked starch (1 gram)
				Cubic centimeters			*Cubic centimeters*
52			5.46	110	100	100	103
52R	52	Washed 10 times with distilled water	4.74	106	96	92	
52L–1	52	0.01-equivalent NaCl; decanted but not washed	6.05	129	117	118	
52L–2	52	0.01-equivalent NaCl; washed 10 times	4.40	158	143	96	
52P–1	52	Moistened with 0.02 per cent NaCl and dried	5.53	83	76	74	
52P–2	52	Moistened with 0.08 per cent NaCl and dried		68	62	60	
52P–3	52	Moistened with 0.24 per cent NaCl and dried	5.58	54	49	50	
52P–4	52P–1	Washed 10 times with distilled H_2O	5.12	88	80	85	
52P–5	52P–2	do		92	83	83	
52P–6	52P–3	do	4.77	103	93	95	
52P–7	52P–5	0.01-equivalent NaCl	5.35	132	120	122	
52C	52	0.01-equivalent HCl	3.21	[1]		30	183
52E	52C	0.01-equivalent NaCl	4.96	[1]		44	105
52U	52C	0.01-equivalent $CaCl_2$	6.18	[1]		40	[2] 50
52D	52	do	6.06	85	77	82	
52F	52D	0.01-equivalent NaCl		132	120	134	

[1] Burst. [2] Partly burst.

Canna sample No. 52R, resulting from washing the original sample No. 52 ten times with distilled water, had a lower pH, swelling power, and viscosity than the original starch, indicating that some of the cations of the air-dried starch were washed out by distilled water.

In sample No. 52L–1 the original starch No. 52 was treated with sodium chloride in the regular way and the excess electrolytes was

poured off but no subsequent washing was done. This resulted in an increase of pH, swelling power, and viscosity. Sample No. 52L–2 was prepared by washing part of sample No. 52L–1 while still wet 10 times with distilled water. In this case the pH dropped below that of sample No. 52, and the swell increased greatly, but the viscosity decreased. This was probably due to the fact that continuous washing removed most of the sodium ion previously substituted in the starch, as was indicated by the low pH. The resultant amylopectin contained a considerable amount of acid amylophosphate which probably had a large swell, but a low viscosity. This is a striking instance in which swell and viscosity failed to agree.

Varying percentages of sodium chloride were added to samples of starch Nos. 52P–1, 52P–2, and 52P–3, with just enough water to moisten them so that distribution would be uniform throughout. In samples Nos. 52P–4 to 6, inclusive, part of the above-mentioned samples were washed 10 times with distilled water and then dried. In samples Nos. 52P–1 to 3, inclusive, the swell and viscosity decreased with increasing strength of sodium chloride. In samples Nos. 52P–4 to 6, inclusive, the opposite was true, the stronger was the previous treatment with sodium chloride, the greater were the swell and the viscosity. Lowering of swell and viscosity when the excess was not washed out was without doubt due to the effect of the excess of electrolytes present. Washing out the excess increased the swell, but the highest value continued below that of sample No. 52, probably because final traces of electrolyte are extremely hard to remove.

In samples Nos. 52E and 52U attempt was made to restore the sodium and calcium ion, respectively, in sample No. 52C, which had previously been washed with dilute acid. The considerable increase in pH in both instances shows that this was accomplished. However, low viscosity and bursting of the granules on heating show that the previous acid treatment had caused them to change irreversibly. In sample No. 52F attempt was made to displace the calcium ion in a calcium chloride treated starch with a sodium ion. This was accomplished as was indicated by the large increase in swell and viscosity.

EFFECT OF REMOVING ELECTROLYTES BY DILUTE ACID AND BY ELECTRODIALYSIS

To determine the effect on swell and viscosity of removing the electrolytes of the starch granules by acid, the starches were treated with a 0.01 and a 0.002 normal solution of hydrochloric acid. The procedure was that described previously (p. 31), in which four treatments with acid were given and three washings were made to remove excess acid.

A 3-chambered cell with parchment paper as the membrane, as described by Humfeld and Alben (*8, p. 992*), was used for the removal of electrolytes by electrodialysis. One hundred and twenty volts were found to effect a rapid extraction of ions. By the use of a water-cooled coil in the central chamber it was possible to maintain the temperature below 35° C. The temperature factor is of especial importance in working with raw starch, because of its tendency to swell at considerably below its so-called gelatinizing temperature. A 50-gram sample of air-dried starch was placed in the central chamber and stirred with 200 cubic centimeters of distilled water. After the cathode and the anode chambers were filled, dialysis was begun.

The starch was stirred at intervals of 10 minutes throughout the experiment, and readings of the amperage were taken. These readings were only approximate because of the large amount of suspended material present. The amperage ranged from 0.02 to 0.04 amperes greater before than immediately after stirring was done. At intervals the contents of the anode and the cathode chambers were withdrawn and titrated with a 0.2-normal acid and base, with phenolphthalein as indicator.

Table 14 gives the results of electrodialysis of five starches.

TABLE 14.—*Amount of cations and anions removed from raw starch by electrodialysis*

Time of electrodialysis	Canna sample 52T (50 grams of sample 52)			Canna sample 24E (50 grams of sample 24)		
	Base N/5	Acid N/5	Amperes	Base N/5	Acid N/5	Amperes
Minutes	*Cubic centimeters*	*Cubic centimeters*		*Cubic centimeters*	*Cubic centimeters*	
1			0.18			0.19
10	1.28	0.26	.17			.06
20			.14			.04
30	.50	.43	.11			
45						.05
60	.18	.12	.06			.04
65						
90	.10	.10	.05			.04
105						
120	.05	.09	.06			.05
Total	2.11	1.00		1.90	0.95	

Time of electrodialysis	Canna sample 5G (50 grams of sample 5)			Potato sample 14F (50 grams of sample 14)			Potato sample 56C (50 grams of sample 56)		
	Base N/5	Acid N/5	Amperes	Base N/5	Acid N/5	Amperes	Base N/5	Acid N/5	Amperes
Minutes	*Cubic centimeters*	*Cubic centimeters*		*Cubic centimeters*	*Cubic centimeters*		*Cubic centimeters*	*Cubic centimeters*	
1			0.18			0.28			0.32
10	1.60	0.31	.10	1.96	0.44	.18	2.80	0.48	.22
20	.31	.15	.09	1.27	.29	.15	.63	.38	.22
30	.26	.17	.07	.76	.31	.10	.10	.20	.14
45	.15	.12	.06	.20	.24	.09			
60	.14	.13	.06	.08	.16	.08	.13	.22	.10
65	.10	.07	.05	.10	.23	.08			
90	.10	.07	.06	.10	.15	.08	.12	.15	.07
105									
120	.05	.12	.06	.02	.16	.07	.04	.11	.07
Total	2.71	1.14		4.49	1.98		3.82	1.54	

Table 15 gives the hydrogen-ion concentration, swell, and viscosity of the acid treated and electrodialyzed starches.

TABLE 15.—*Effect of removing electrolytes by washing with dilute acid and by electrodialysis*

CANNA STARCH

Laboratory No.	Treatment	pH of raw starches	Swelling power	Relative swell (original starch as 100)	Relative viscosity (original starch as 100)	Swell of uncooked starch (1 gram)
			Cubic centimeters			*Cubic centimeters*
52	None (original starch)	5.46	110	100	100	
52C	0.01-equivalent HCl	3.21	[2]		20	183
52S	0.002-equivalent HCl	3.68	[2]		30	101
52T	Electrodialyzed	3.51	[2]		30	[1] 37
24	None (original starch)	7.01	68	100	100	
24E	Electrodialyzed	3.94	73	107	71	
5	None (original starch)	7.28	66	100	100	
5D	0.002-equivalent HCl	3.70	[2]		30	78
5G	Electrodialyzed	3.66	68	103	66	

POTATO STARCH

14	None (original starch)	6.76	100	100	100	
14E	0.002-equivalent HCl	3.49	[2]		40	[1] 38
14F	Electrodialyzed	3.62	[2]		40	[1] 45
56	None (original starch)	6.06	155	100	100	
56C	Electrodialyzed	3.52	[2]		40	[2]

[1] Supernatant liquid milky with many suspended fragments, but with a definite dividing line.
[2] Granules burst. No dividing line apparent between settled granules and supernatant liquid.

Electrodialysis of raw starches is effective in removing appreciable amounts of both cations and anions. The cations come off very rapidly, approximately 50 per cent of those removed in two hours being dialyzed in the first 10 minutes. The anions dialyze much more slowly. At first the cations greatly exceeded the anions, but later the anions exceeded the cations, the canna starches requiring 60 to 90 minutes, and the potato starches 30 to 45 minutes. From these data it seems probable that electrodialysis would be effective in removing a large part of the cations of the starch granule and that the anions would continue to dialyze slowly for an indefinite period.

The difference between the canna and the potato starches is pronounced. The latter far exceeded the former both in total base and in acid. A distinction was also apparent between the high and the low viscosity starches in each species, the low canna sample No. 5 and potato sample No. 14 exceeding the high canna sample No. 52 and potato sample No. 56 in both base and acid. Canna sample No. 24 from stored canna rootstocks resembled sample No. 52 in this respect.

Table 15 shows the striking effect on the starch granules of partly removing the cations and the anions by dilute acid and by dialysis. Each method resulted in a decided lowering of the pH and a loss of viscosity.

Except for sample No. 52C, which was treated with a hundredth-normal hydrochloric acid solution, removal of the electrolytes either by acid or by electrodialysis did not result in any appreciable increase in swell in the uncooked starch and usually the granules burst during cooking. Bursting of the granules is easily apparent in the determination of the swell. The supernatant liquid is opalescent, and

angular particles of the amylopectin are to be seen floating about in it. Where all the granules are ruptured, as in potato sample No. 56C, there is no dividing line, the solution becoming increasingly opalescent in progressing downward, with a few cubic centimeters of dense amylopectin at the bottom. Where only part of the granules are broken, a dividing line is apparent, as in canna sample No. 52T and in potato samples Nos. 14E and 14F. The volume is then, of course, abnormally low.

Results of altering the nature and the amount of electrolytes naturally occurring in starches are so pronounced as to leave no doubt regarding the essential nature of their occurrence in the starch granule. This is especially well brought out by the fact that electrodialysis in which no chemicals are used—so that the only possible change is the removal of the electrolytes—completely alters the essential properties of the granule. Treating with a hundredth equivalent of salts in the cold shows a marked effect and is equally convincing evidence that a considerable part of the cations exists at or near the surface of the granule and is easily displaced. Moreover, the fact that treatment with monovalent ions greatly increases swell and viscosity of raw starches, whereas adsorbed electrolytes tend to decrease them, would seem to indicate that in the former case a chemical combination exists with the starch granule.

Samec (*17, p. 18*) states that the ability of the amylopectin to swell and become viscous is dependent upon the phosphoric acid ester structure. Removal of the phosphoric acid causes less of this property. Qualitative tests showed that a certain amount of phosphoric acid was removed by treating the starch granules with salts and acids and by electrodialysis. The properties of the treated starches are thus the result of a change of cations and the removal of a certain amount of the phosphoric acid present. In the starches treated with salts the latter effect is probably very small. In electrodialysis and probably in acid treatment it is much more pronounced. Probably, therefore, the drastic action of these two treatments is due to removal of both the cations and the phosphate ion. The fact that in almost every case cooking caused nearly all the starch granules to burst, whereas in the uncooked swell many of the granules remained intact, indicates that the removal of the electrolytes tended to weaken the starch envelope rather than to cause rupturing.

These data also give some possibly significant differences between swell and viscosity. Attention has already been called to canna sample No. 52L–2 (Table 13), in which washing out the cation caused the swell to exceed that of the original starch by 43 per cent while the viscosity was 4 per cent less. In canna samples Nos. 24E and 5G (Table 15) electrodialysis increased the swelling power to 107 and 103 per cent, respectively, and decreased the viscosity to 71 and 56 per cent, respectively, as compared with the original starches. This possibly indicates that viscosity may be dependent upon an intergranular structure which is destroyed upon the removal of the cation.

INVESTIGATION OF CAUSES OF VARIATION IN PROPERTIES OF STARCHES OF THE SAME SPECIES

It is well understood that starches from the same species vary in properties depending on the conditions of climate and soil under which the plants are grown. Even when starch-producing plants are grown

in the same locality where, presumably, conditions are fairly constant for growth the resulting product will be found to vary decidedly in viscosity. The cause of such variation has yet to be determined.

Changing the nature or the amount of cations in the starch gave such pronounced results as to suggest the possibility that the change itself is the cause of variation. It has been repeatedly stated that the cations naturally existing in starch may be replaced by the salts occurring in the water used in manufacturing. Tryller (*20*) found potato starch prepared with distilled water to contain 0.01 per cent of lime (CaO), 0.07 per cent of potash (K_2O), and 0.007 per cent of soda (Na_2O); and that prepared with tap water to contain 0.095 per cent of lime, 0.009 per cent of potash, and 0.07 per cent of soda. The tap water thus increased the percentage of total cations and at the same time greatly increased the calcium content. The replacement of potassium by sodium would have no appreciable effect on viscosity, but any increase in calcium would probably have a decided effect.

DIFFERENCE IN ELECTROLYTES

Two methods were used to determine the relative differences in the cations and the anions removed from the different starches. In the first method 50 grams of each starch was electrodialyzed for two hours, as described previously (p. 39), and the calcium and the phosphorus were determined in the dialysate. In the second method 50 grams of each starch and 100 cubic centimeters of normal sodium chloride solution were placed in glass tubes each 1 inch in diameter and 18 inches in height, and percolation was allowed to go on all night. The entire percolate of the unwashed starch was analyzed for calcium and for phosphorus. Table 16 gives the amounts of calcium and of phosphorus obtained by electrodialysis and displacement with sodium chloride.

TABLE 16.—*Relation of the amounts of calcium and phosphorus removed by electrodialysis and displacement by normal NaCl solution from 50-gram samples of four starches* [1]

REMOVED BY ELECTRODIALYSIS

Starch and sample No.	pH	Amount of N/5 cations	Amount of CaO	CaO equivalent in N/5 solution	Amount of monovalent bases N/5 [2]	Amount of P_2O_5
Canna:		*Cubic centimeters*	*Grams*	*Cubic centimeters*	*Cubic centimeters*	*Grams*
52		1.82	0.0000	0.00	1.82	0.0038
26		2.35	.0054	.48	1.87	.0011
5		1.99	.0011	.10	1.89	.0018
Potato:						
14		4.17	.0190	1.70	2.47	.0047

NaCl DISPLACEMENT

Canna:						
52	5.66		0.0012			0.0025
26	6.66		.0126			.0011
5	6.47		.0068			.0014
Potato:						
14	6.43		.0300			.0030

[1] Sample No. 26 was similar to sample No. 24 except that the rootstocks of the former were stored for 27 days instead of 19 days, before the starch was extracted from them.

[2] Amount of N/5 cations minus CaO equivalent in N/5 solution.

Table 16 brings out significant differences in the starches under the two methods of extraction. Electrodialysis removed somewhat more phosphoric acid than did the sodium chloride displacement, whereas the latter removed considerably more calcium. However, the relative differences between the four starches were the same with the two methods. Canna sample No. 52, from fresh rootstocks, contained very small amounts of calcium, whereas canna sample No. 26, from rootstocks grown in the same locality but stored for 27 days, contained considerable amounts. Canna sample No. 5, from fresh rootstocks grown at low altitude, had decidedly more calcium than did sample No. 52, but less than sample No. 26. Potato sample No. 14 contained much more calcium than did any of the canna starches. The canna starches were in exactly reverse order as regards phosphoric acid and calcium. Sample No. 52 contained the greatest amount of phosphoric acid, and sample No. 26 the least, while the latter contained the greatest amount of calcium and the former the least. Potato sample No. 14 also contained more phosphoric acid than any of the canna starches. Assuming that calcium is the only cation other than the monovalent bases in the starches, subtraction of the calcium from the total cations gives a nearly constant quantity of monovalent bases in all three starches. The difference in the extracted bases was thus mainly in the amount of calcium.

The data given above can be considered as having only relative value since they do not represent the total quantities of either anions or of cations. Especially is this true of the phosphoric acid which represents only a small part of the total. With the cations it seems probable that the figures come nearer to the total or at least to the replaceable cations. The amount of calcium occurring in sample No. 26 would probably be sufficient to account for the loss in viscosity when one considers the marked depressing effect of this bivalent ion on sample No. 52. If the phosphoric acid data are taken as significant, phosphates also may have been lost during storage of the rootstocks. According to Samec (*17, p. 18*) this loss would decrease viscosity. The fact that the two unlike methods gave essentially the same differences lends support to the belief that within a single species the electrolytes have an important influence on the variations in viscosity of the natural starches.

DEGREE OF SATURATION OF STARCH WITH CATIONS

To determine the amount of alkali required to neutralize a given sample of starch, Rosenthaler (*16*) refluxed the starch on a water bath with an excess of standard alcoholic sodium hydroxide and back titrated the excess of alkali with standard acid. Grimshaw (*4*) gives the method used by various commercial concerns as that of titrating the raw starch with standard alkali, using in some instances phenolphthalein and in others methyl orange as indicator. It was found difficult to use this method because of the gradual change in the end point. The method finally adopted was that of electrotitration, with the quinhydron electrode. Ten grams of starch in 50 cubic centimeters of water was used for the determination. It was necessary to keep the starch in complete suspension throughout the titration. After each addition of standard alkali the solution had to be stirred for several minutes before a fairly constant end point was reached.

Table 17 gives the initial hydrogen-ion concentration and titration values of the four starches. The latter are expressed as cubic centimeters of tenth-normal sodium hydroxide solution necessary to bring 100 grams of the starch to a pH of 7.

TABLE 17.—*Hydrogen-ion concentration and degree of saturation of starches*

Starch and sample No.	Initial pH of starch	Amount of N/10 NaOH to neutralize 100 grams of starch
Canna:		
52	5.46	7.9
5	7.28	0
56	6.06	9.1
Potato starch:		
14	6.76	.6

Table 17 brings out appreciable differences in the four starches. Canna sample No. 52 and potato sample No. 56, each with a low pH, are relatively unsaturated, whereas canna sample No. 5 and potato sample No. 14 are practically neutral. Samec (*17, p. 136*) states that the acid end point allowable for market specifications is 6 cubic centimeters of a tenth-normal solution of sodium hydroxide. Wolff (*22, p. 1003*) states that normal potato starch requires 6 cubic centimeters of potassium hydroxide for neutralization. In the above-mentioned starches the unsaturated samples (Nos. 52 and 56) represent the strongest, and the saturated samples (Nos. 5 and 14) the least viscosity. A consideration of the significance of the degree of saturation would seem to indicate that the valence of the cation rather than the degree of saturation has the predominating influence. If the increase in degree of saturation is due to calcium, as often happens in the manufacturing process, the viscosity should decrease. If, on the other hand, the increase is due to sodium or to potassium the viscosity would probably be greater.

From the data given in Tables 16 and 17 it seems probable that variations in the amount and kind of cations may account for at least a part of the differences occurring in commercial starches. The higher degree of saturation and the larger amounts of calcium in the low-viscosity starches suggest that this may be the most frequent cause of decrease in viscosity. Starch appears to have a greater affinity for calcium than for sodium or potassium. For example, in Table 13 sample No. 52, which had been freed from cations by washing with hydrochloric acid, had a pH of 4.98 in sample No. 52E when treated with sodium chloride, and a pH of 6.18 in sample No. 52H when treated with calcium chloride. Numerous investigators have found that small amounts of calcium in the water used in the manufacturing process cause considerable increase of calcium in the finished starch. The failure of the low viscosity starches to increase to the viscosity of the high viscosity starches when treated with monovalent salts may have been due to the fact that the salts affect only a part of the cations of the starch granule, as is shown by the progressive increases in viscosity with higher concentrations of electrolyte and number of treatments. It is also probable that other

factors than cations enter into the capacity of a starch to swell, for example, the amount of phosphoric acid, the relative proportion of amylose and amylopectin, and the like.

The ease with which the viscosity of a starch may be changed is a matter of possible practical importance. It appears that the relative fluidity or viscosity of a starch may be changed as desired by the selection of an electrolyte of proper kind and strength. Dried starch need not be used. Treatment with salts might be made a regular part of the refining in the manufacturing process, the wet starch being treated with the salts and subjected to two additional washings. When the water used in manufacture contains too much calcium, the addition of sodium chloride in sufficient quantities should prevent the formation of a calcium starch. It is possible that this substitution of cations in the natural starch might weaken the granules so that they would burst more easily.

SIZE OF STARCH GRANULES

Originally it was thought that the size of the granule determined the viscosity of the starch, the larger the granules the greater the viscosity of the starch. Later work indicates, however, that the opposite is true. Naudain (*12*) states that wheat containing the smaller-grained starches makes the stronger flour. Wolff (*22, p. 1003*) took potato starch from the upper and the lower part of the flume. He found generally little difference in viscosity due to size of granule, although the smaller granules sometimes gave the higher viscosity.

Of the commercial samples of potato starch examined one was outstandingly high and another outstandingly low in viscosity. Sample No. 31 of high viscosity was a starch imported from the Netherlands, and sample No. 18 of low viscosity was a domestic starch. Microscopic examination showed that the low-viscosity starch was much smaller grained than the other. To determine if this difference in granule size was the cause of difference in viscosity, 30 grams of the air-dried starch was placed in an elutriator of the Hilgard type and elutriated with water flowing at the rate of 170 cubic centimeters per minute. Table 18 shows the distribution of starch according to size of granules and the viscosity of each fraction. The viscosity measurements were made with a pipette viscosimeter. Results are expressed as relative viscosity (water=1). A 1.4-gram sample of starch was used in each determination.

TABLE 18.—*Relation between viscosity and size of granules of a high and a low viscosity potato starch* [1]

Average size of granules	Sample No. 18 (domestic starch of low viscosity)		Sample No. 31 (Dutch starch of high viscosity)	
	Proportion of starch	Relative viscosity (water=1)	Proportion of starch	Relative viscosity (water=1)
Millimeters	*Per cent*		*Per cent*	
0.07	15.1	1.6	31.9	3.0
0.06	27.5	2.6	31.2	3.3
0.04	19.7	2.4	18.2	3.8
0.03	15.6	3.8	11.1	5.0
0.025	22.1	5.0	7.6	6.8
Whole sample		2.6		5.2

[1] The potato starches used in this test were not the same as those used in previous tests.

Very pronounced differences were apparent in the two starches. In the low-viscosity domestic starch 22.1 per cent of the granules were of the smallest size, and in the high-viscosity Dutch starch only 7.6 per cent. In the larger granule fractions the Dutch exceeded the domestic starch in viscosity. In both kinds there was a gradual increase in viscosity with decreasing size in the three classes (0.07 to 0.04 millimeter, inclusive), and then a very rapid rise in the next two classes. It is significant, however, that the viscosity of each class of granules of the high-viscosity starch exceeded that of the corresponding class of the low-viscosity starch. This shows that while the small granules in any given starch may exceed the large in viscosity, it does not follow that a small-granuled starch should for this reason exceed a large granule in viscosity.

BROKEN GRANULES

Since viscosity is dependent upon the proportion of unbroken granules, any difference in the amount of injured or ruptured granules in the raw starch would result in a difference in viscosity. To find the approximate amount of broken granules, soluble amylose was determined in the supernatant liquid from determinations of the swelling power of a number of starches. Table 19 gives the relative amounts expressed as percentage in the starch.

TABLE 19.—*Relative amounts of broken granules (soluble amylose) in different starches*

Starch and sample No.	Description	Swelling power	Proportion of soluble amylose
		Cubic centimeters	*Per cent*
Canna:			
52	High viscosity	107	12.4
20	Medium viscosity	86	11.0
24	Low viscosity	67	9.7
Potato:			
56	High viscosity	156	6.8
14	Medium viscosity	95	7.6
55	Low viscosity	63	6.4

Broken granules evidently were not the cause of differences in viscosity in these starches. In fact, the high-viscosity canna starches contained the largest amount of soluble amylose.

POSSIBLE SIGNIFICANCE OF STARCH ELECTROLYTES IN PLANT METABOLISM

The relative ease with which the cations of the starch granules are given off to, or taken up from, the solution suggests the possibility of considerable cation exchange taking place within the plant cell itself. It seems possible that the cation phosphoric acid ester complex of the starch granule is in equilibrium with the electrolytes of the cell sap. Since the latter changes in nature and in composition under the influence of many factors of environment, the starch might well show corresponding changes in its electrolytes. Considering the very appreciable amounts of phosphorus, potassium, and calcium in the starch granule, and the large proportion of starch in the storage organ of the plant, it seems possible that the starch granule electrolytes play a significant rôle in the mineral metabolism of the plant cell, not only as a means of mineral storage for new growth, but also as

a cell sap buffer to maintain equilibrium in hydrogen-ion concentration values and concentration.

SUMMARY

The present investigation was undertaken principally to compare the properties of edible-canna and potato starches and to study the causes of differences in the properties of starches of the same origin.

Differences in the swelling power, viscosity, and hydrogen-ion concentration of the starches were determined. New methods were devised for each of these determinations. A new method was also devised for the preparation of the starch solution. In this method hot water is added to a starch suspension in such a way as to make it possible to measure swelling of the starch granules without stirring or agitation and with a minimum of broken granules.

Swell and viscosity were found not to be directly proportional. A fair agreement was obtained by plotting the viscosity against the product of the concentration and swell.

Determinations of hydrogen-ion concentration in the water extract of starches proved to be unreliable.

Electrometric measurement of the starch suspension was found to be a very satisfactory method.

The effect of different neutral salts on swell and viscosity was found to be proportional to the valency of the cation, the greater the valency the greater the depression of swell and viscosity. The anions had little effect. Sodium hydroxide produced initial increase with subsequent decrease.

Substitution of monovalent cations in the raw starches greatly increased the swell and viscosity of all the starches. Bivalent cations generally caused a decrease. Trivalent cations caused a very large decrease. Removal of the cations by acid and electrodialysis caused the granule to burst when cooked.

Investigation of the causes of differences in starches of the same kind showed that the starches of greatest swell and viscosity were unsaturated as to cations and had a low pH. Analysis of the electrolytes removed by electrodialysis and displacement with sodium chloride showed that the low-viscosity starches contained appreciably more calcium than the high-viscosity starches. The possibility of preventing substitution of calcium in the starch granule either in the process of manufacture or during the growth of the plant is suggested. Difference in size of granules, or in amount of broken granules, was not found to be the cause of difference in viscosity in the starches used.

Comparison of the properties of edible-canna and potato starches showed that the latter is probably somewhat superior to the former in swell and viscosity. Potato starch is also characterized by decidedly larger amounts of cations and of phosphoric acid than is edible-canna starch. In their general properties, the two starches are similar.

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